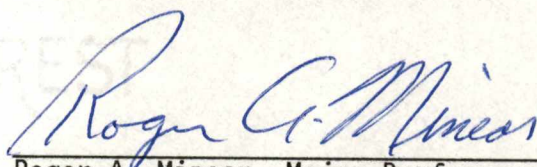


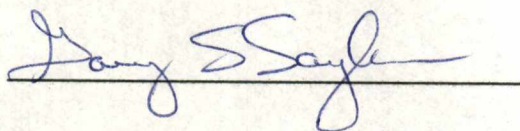
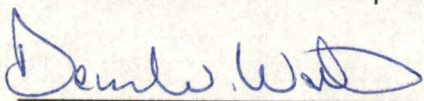
To the Graduate Council:

I am submitting herewith a thesis written by Douglas Edward Johnson entitled "The Effects of Coal Particle Size and the Percentage of Coal Present in the Slurry on the Leaching of Organic Compounds from Wyodak Coal." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

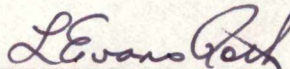


Roger A. Minear, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Vice Chancellor
Graduate Studies and Research

THE EFFECTS OF COAL PARTICLE SIZE AND THE PERCENTAGE
OF COAL PRESENT IN THE SLURRY ON THE LEACHING OF
ORGANIC COMPOUNDS FROM WYODAK COAL

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Douglas Edward Johnson

June 1981

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ABSTRACT

The effects of coal particle size and the percentage of coal present in the slurry on the leaching of organic compounds from Wyodak coal was determined using analysis of variance.

The initial nonvolatile (NVTOC) ranged from 40 to 387 ppm and the extraction NVTOC ranged from 26 to 362 ppm. Coal particle size had no affect on these nonvolatile TOC concentrations while the percentage of coal present in the slurry did. As the percentage of coal present in the slurry increased, the NVTOC levels also increased.

Three peaks representing organic compounds extracted from the coal leachate were analyzed and separated using high performance liquid chromatography. Peaks 1, 2, and 3 eluted from a C18 HPLC column at 1.5, 3.5, and 15 minutes, respectively. The normalized peak responses were; Peak 1: 0.08 to 12.0, Peak 2: 0.0 to 12.0, and Peak 3: 0.0 to 1.13. ANOVA results indicate that coal particle size significantly affected the normalized responses of Peaks 1 and 3, but this affect was not clear.

The percentage of coal present in the slurry was found to affect the normalized responses of all three peaks and the Total Peak response. Generally as the percentage of coal present in the slurry increased, the peak responses also increased.

Molecular weight analysis indicates that most of the organic compounds present in the coal leachate are of relatively low molecular weight ($\cong 100$).

Based on HPLC analyses, molecular weight analyses, and the structure of coal itself, most of the organic compounds present in the

leachate are probably heteroatom (oxygen, nitrogen, and sulfur) containing aromatic compounds of relatively low molecular weight ($\cong 100$).

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I. INTRODUCTION

The National Energy Plan (NEP) introduced by President Carter in April 1977 emphasizes the increased usage of coal in order to meet the nation's future energy needs. This shift in coal's importance as a major energy source has brought attention to potential pollution hazards associated with coal. One such hazard is the leaching of trace organics from coal stored in reserve storage piles and coal transported in slurry pipelines.

Coal storage is usually divided into two types according to purpose; live or active storage and reserve or inactive storage. Live storage is fed directly into firing equipment and is usually under cover. Reserve coal is stored outdoors and is usually referred to as the stockpile or coal pile.¹ The reserve pile is thus exposed to weathering effects such as rain, sleet, or snow, which cause the leaching of trace organics from coal.

The size of these reserve piles vary and is usually determined by the size of the plant. Typically these piles are 8-12 meters in height and cover an area between 60,000-300,000 square meters. Usually 600-1800 cubic meters of coal are required for every megawatt of rated capacity.² A coal pile covering an area of 100,000 square meters would be exposed to 100,000 cubic meters of water annually with an annual rainfall of one meter. Since there are approximately 900 reserve piles in the United States, the runoff from these coal piles presents a potential danger of surface and underground water contamination.³

Another potential problem similar to coal pile drainage is the wastewater which occurs from dewatering coal transported in slurry pipe-

lines. Current technology allows the coal to be transported to a power plant in a slurry of 50% coal and 50% water. Approximately 25% of the water is removed from the coal at the power plant by gravity, vacuum filters, centrifuges or a combination of the three methods.⁴

Presently there is only one coal slurry pipeline operating in the United States, the Black Mesa Pipeline, which transports 4.4 million metric tons of coal annually. Six additional pipelines with a total capacity of 87.4 million tons per year are in the planning stage.⁴ Using 50% coal slurry and 25% dewatering capacity as operating standards, a total of 13.2 million cubic meters per year of wastewater must be disposed of properly to avoid surface and groundwater contamination when these lines are operational.

The wastewaters from coal storage piles and coal slurries are similar in that exposure of coal to water initiates the oxidation of pyrite to form sulfuric acid and consequently an acidic environment. This environment facilitates the leaching of metals, trace elements, and possibly organic compounds from the coal. Differences between the two wastewaters may occur due to differences in the amount of water and oxygen the coals are exposed to in the pile and in the pipeline. Coal transported in pipelines is exposed constantly to a water inundated environment which becomes anaerobic as dissolved oxygen present in the water reacts with the pyrite. This may affect the leaching of metals, trace element, and organic compounds. Coal stored in piles has an unlimited access to oxygen and is not exposed to a constantly inundated environment. However, under heavy rain conditions, coal located deeper in the pile may be exposed to conditions similar to coal transported in pipelines.

While previous analysis of coal pile leachates (CPL) and coal slurry leachates (CSL) have been concerned with the presence of general organic parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC), national concern exists for the identification of trace organic compounds that may be hazardous to the environment.

In the draft environmental impact statement for the Coal Research, Development, and Demonstration Program, the Energy Research and Development Administration (ERDA) addressed the probable water quality problems associated with the increased utilization of coal in the United States.⁵ ERDA identified two potential environmental concerns; (1) the presence of potentially toxic and carcinogenic organic compounds in coal residues and products, and (2) the potential presence of trace metal pollutants in the products and by products.

In October 1974, the United States Environmental Protection Agency (EPA) issued guidelines for six wastewater sources in electrical generating plants. These sources are fly ash slurries, cooling tower and boiler blowdown, coal pile and floor drain runoff, and sanitary wastes. As far as coal pile leachate is concerned, only two standards have been established, total suspended solids (TSS) of less than 50 parts per million (ppm), and a pH between 6.0-9.0; no standards have been set for the wastewater from slurry pipelines.⁶ However, in section 307 of Public Law 92-500 of the Water Pollution Control Act (WPCA), the Environmental Protection Agency (EPA) was required to publish a list of toxic pollutants and effluent standards concerning any toxic pollutants or combination of toxic pollutants taking into account the toxicity of the pollutant, its persistence in the environment, and degradability. EPA

has since been stalled in their efforts to implement section 307 due to technical uncertainties, lack of information, and legal complications.⁷ As soon as this list is established, coal pile and coal slurry leachates may be subject to its parameters.

These two wastestreams must also meet effluent limitations established in section 301 of the Water Pollution Control Act. This section required that by July 1, 1977, power plant discharges were to meet effluent limitations corresponding to those attainable by the best practical control technology (BPCTA). Section 301 also requires that by July 1, 1983, treatment of power plant discharges shall require the best available technology economically achievable (BATEA).

Rice and Strauss have presented information concerning coal pile leachate from several power plants. They state that the Federal Water Pollution Control Act Amendment of 1972 has brought about some fundamental changes in the manner in which power generation facilities discharge chemical wastes, and that coal pile runoff is another waste stream which needs to be contended with.⁸

Experimental Objectives

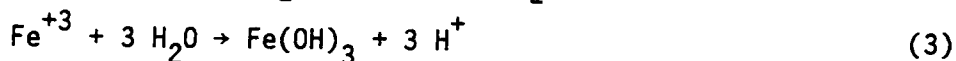
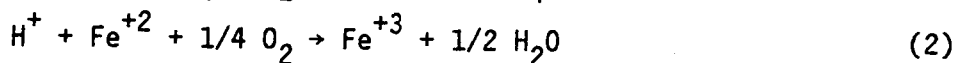
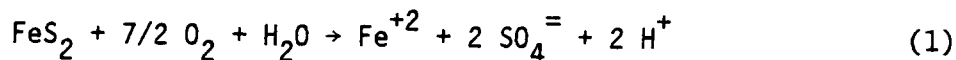
The main objectives in this study were; (1) determine whether or not coal particle size and the percentage of coal present in the slurry significantly affect the leaching of organic compounds from Wyodak coal, (2) characterize what type of compounds are being leached from Wyodak coal, and (3) propose possible treatment schemes for removing the organic compounds from the leachate.

II. LITERATURE REVIEW

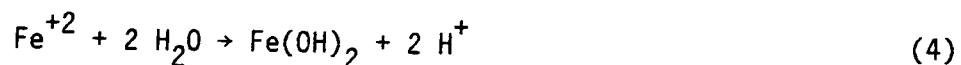
Since the leachate from coal associated with coal storage piles and coal slurry pipelines represents a potential source of environmental pollutants (both organic and inorganic), this literature review was designed to assess existing information concerning (1) the chemistry involved in the leaching of pollutants from coal, (2) the effects of various parameters (coal particle size, percentage of coal present in the slurry, etc.) on the leaching of these pollutants from coal, (3) the structure of coal which provides an insight as to what type of compounds may be leached from coal, and (4) an overall view of the concentration ranges of various organic and inorganic constituents found in coal leachate.

A. Oxidation of FeS_2

The oxidation of pyrite (FeS_2) has an important influence on the organic and inorganic constituents present in the coal leachate. The oxidation of FeS_2 produces sulfate and hydrogen ions; the latter reacts with metals, trace elements, and organic compounds present in coal causing their dissolution into the leachate. The iron cycle in coal pile and coal slurry leachate can be represented by the following equations.⁹



Two additional reactions may occur involving Fe(II). First, Fe(II) may precipitate as the hydroxide.¹⁰



Or it (Fe(II)) may precipitate a ferrous carbonate.¹¹



Figure 1 shows the solubility of ferrous iron in the presence of 100 ppm total carbonate (as CaCO_3). It can be seen from this graph that ferrous hydroxide will only precipitate above pH 8.0 while ferrous carbonate may precipitate in neutral or acid pH. Since the pH of coal pile and coal slurry leachates is rarely above 8.0, reaction (4) is not likely to occur.

B. Oxidation Rate Laws Governing Fe(II) Oxidation

Two rate laws have been established for the oxidation of ferrous iron. In the acid region below pH 4.0 the rate is first order in Po_2 and is independent of pH.

$$\frac{-d(\text{Fe}^{+2})}{dt} = k [\text{Fe}^{+2}]^n \text{Po}_2 \quad (6)$$

This reaction may be first or second order depending on the solution the reaction takes place. In phosphate, pyrophosphate, and concentrated sulfate solutions, the reaction is first order while in perchlorate and dilute sulfate solutions, the reaction is second order.^{9,12,13,14}

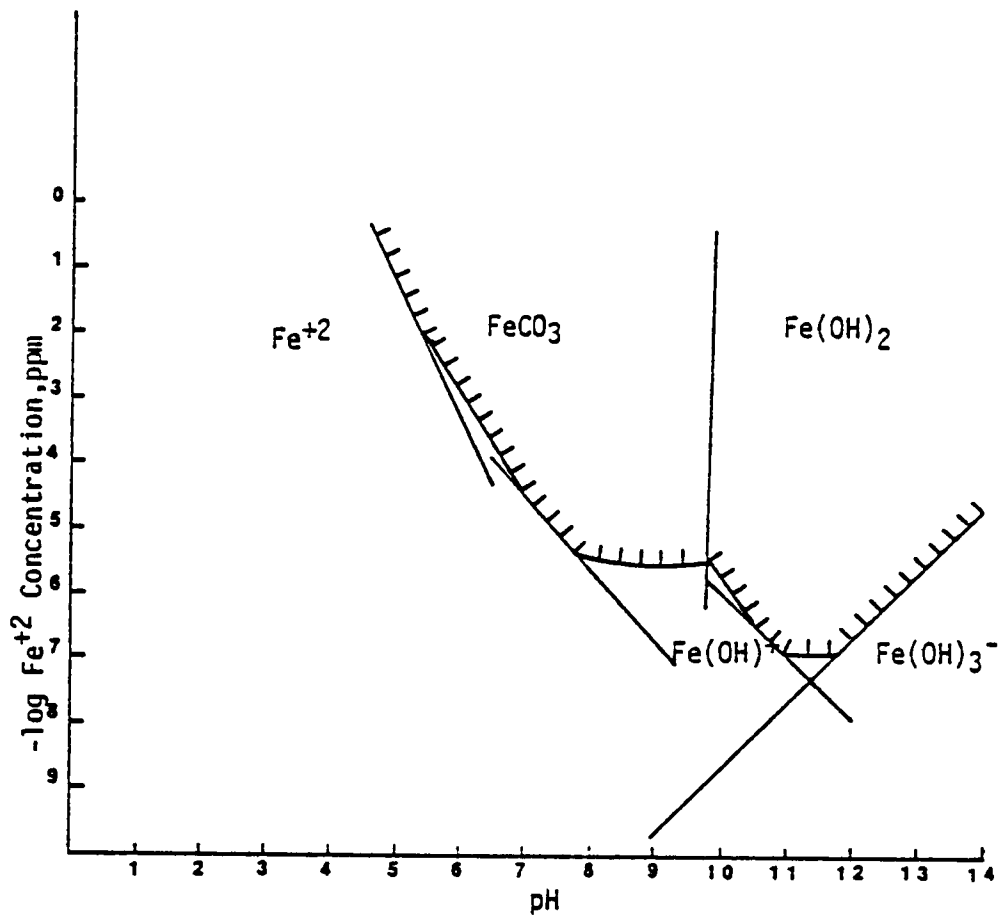


Figure 1. Solubility of ferrous iron in water containing 10^{-3}N total carbonate.

In bicarbonate buffered solutions, with iron concentrations below 1 ppm, the rate law is:¹⁵⁻²⁰

$$\frac{-d[\text{Fe}^{+2}]}{dt} = k [\text{Fe}^{+2}] [\text{OH}]^2 \text{Po}_2 \quad (7)$$

Based on studies in bicarbonate buffered systems with varying alkalinities, Wheeler modified equation (7) to include an alkalinity term.²¹

$$\frac{-d[\text{Fe}^{+2}]}{dt} = k [\text{Fe}^{+2}] [\text{OH}]^2 [\text{Alk}]^{-.75} \quad (8)$$

Several constituents in coal pile and coal slurry leachates have been found to influence the rate constants in equations (7) and (8).

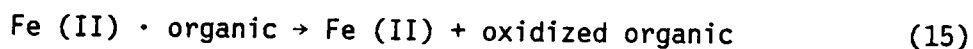
Copper has been studied in both acid and neutral solutions. Chen and Davidson observed in acid solutions that copper in concentrations as low as 60 ppb catalyzed the reaction.⁹ Stumm and Lee observed catalytic effects in bicarbonate buffered solutions for copper concentrations as low as 60 ppb while Wheeler observed catalytic effects for concentrations as low as 24 ppb.^{15,21}

The effect of bicarbonate on the rate constant is unclear. In solutions oversaturated with respect to ferrous carbonate, Jobin and Gosh observed a catalytic effect on the rate constant while Singer was not able to develop an expression for the catalytic effect.²² Wheeler, however, observed a negative effect on the reaction rate.²¹

The effect of sulfate on the reaction rate is dependent upon the acid concentration. In concentrated acid solutions, Huffman found that the reaction is catalyzed by sulfate.¹³ Singer and Stumm found that the rate decreased with increasing sulfate concentrations at pH 3.0 for sulfate concentrations as low as 1.0 mg/l.²³ However, at pH 6.0-8.0 no

effect is observed for sulfate concentrations as large as 10 mg/l. Wheeler did not observe any catalytic or negative effects for sulfate concentrations as large as 1000 mg/l.²¹

It has been confirmed by Singer and Jobin and also Wheeler, that ferrous iron is stabilized by hydroxylated hydrocarbons such as humic acid. Because iron is stabilized by these specific compounds, large quantities of other organics may be present without being affected by iron. Hem found that ferrous iron-tannic acid complexes were much weaker than complexes with ferric iron.²⁴ Stumm proposed that the ferrous iron acts as a catalyst for the oxidation of the organic compound. The following equations were proposed by Stumm to explain this behavior.



The exact mechanism for the stabilization of ferrous iron has not been worked out yet, however, three interactions have been considered; (1) peptization of the organic molecule by charged hydroxy-ferric iron complexes, (2) chelation of the metal ion (ferric or ferrous) by the humate ligand leading to the formation of polynuclear complexes, and (3) reduction of ferric iron to ferrous iron by the humic substances, thereby generating the more soluble form of iron.²⁵⁻³¹

C. Effects of Various Parameters on Coal Leachate Quality

FeS₂ Concentration

The production of acidity [see equations (1) and (3)] resulting from the oxidation of FeS₂, initiates the leaching of metals and trace elements from coal. In acid environments, these constituents become

soluble and leach into the water. Since the amount of acidity produced is a direct function of pyritic sulfur concentration, the concentration of heavy metals and trace elements in the leachate will also be direct functions of the pyritic sulfur content in coal. Several investigators have observed this correlation.^{32,33,34}

It has been observed that coals from different geographical regions contain different amounts of sulfur. The interior province coals and most Appalachian coals were formed under the influence of high sulfate ion concentrations in saline water. As a result these coals contain high concentrations of sulfur (>3%). Western coals were formed under freshwater conditions and contain low sulfur concentrations (<1.0%).³⁵ The leachate from facilities handling the low sulfur western coals should contain lower concentrations of heavy metals and trace elements and have a higher pH when compared to leachates from facilities handling eastern coals. Figures 2, 3, and 4 show the sulfur content of bituminous, subbituminous, and lignite coals from each of the U.S. provinces.

Additional differences between western and eastern coals occur in the trace element content as shown in Tables 1 and 2.³⁶ Table 1 shows that Eastern Interior coals have higher concentrations of beryllium, boron, titanium, vanadium, chromium, gallium, germanium, molybdenum, and tin while Western Interior coals have higher concentrations of cobalt, zinc, and lanthanum. As far as hazardous trace elements are concerned (see Table 2), Eastern Interior coals have higher concentrations of mercury, lead, and zinc while Western Interior coals have higher concentrations of antimony, arsenic, beryllium, and selenium; Appalachian coal is also high in beryllium. The lowest concentrations of hazardous trace elements is found in Power River Basin coals located in Wyoming and Montana.

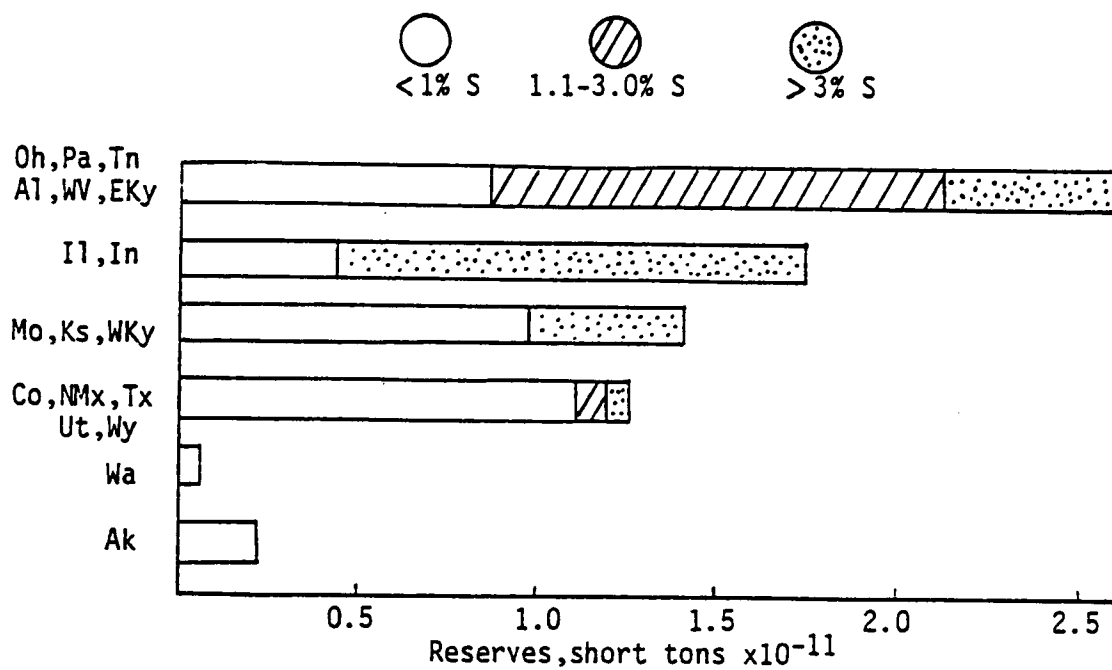


Figure 2. Distribution of U.S. bituminous coals by geological province and sulfur content.

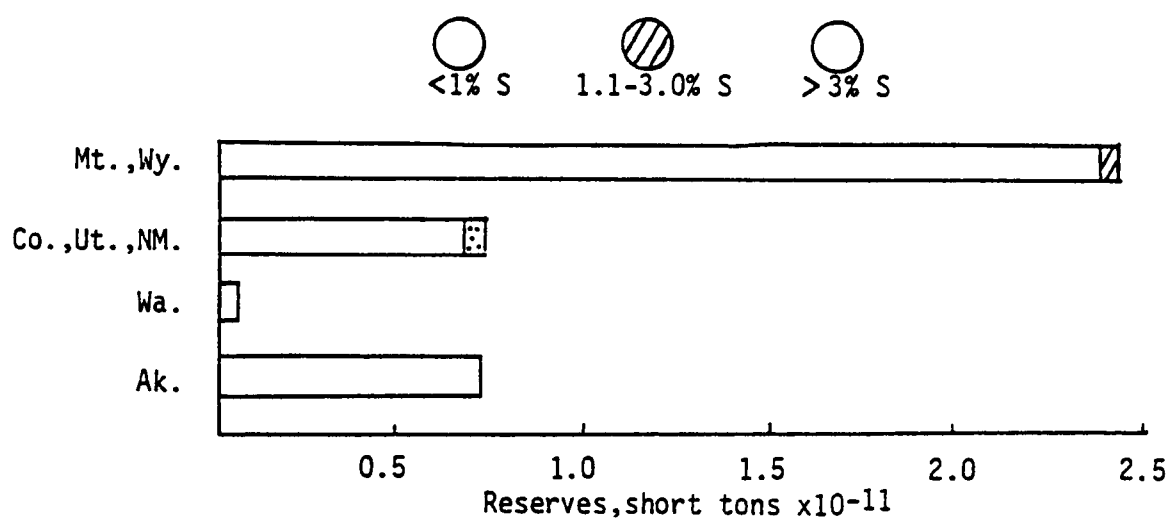


Figure 3. Distribution of U.S. subbituminous coals by geological province and sulfur content.

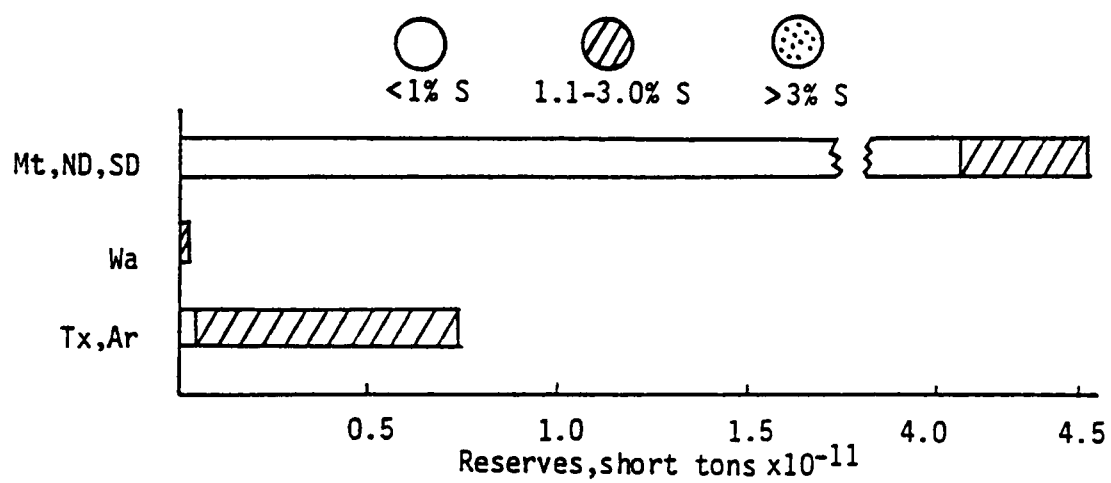


Figure 4. Distribution of lignite coals by geological province and sulfur content.

Table 1. Trace-element Content of American Coals (ppm in coal)

Element	Region			
	Northern Great Plains	Western Interior	Eastern Interior	Appalachian
Beryllium	1.5	1.1	2.5	2.5
Boron	116	33	96	25
Titanium	591	250	450	340
Vanadium	16	18	35	21
Chromium	7	13	20	13
Cobalt	2.7	4.6	3.8	5.1
Nickel	7.2	14	15	14
Copper	15	11	11	15
Zinc	59	108	44	7.6
Gallium	5.5	2.0	4.1	4.9
Germanium	1.6	5.9	13	5.8
Molybdenum	1.7	3.1	4.3	3.5
Tin	0.9	1.3	1.5	0.4
Titrium	13	7.4	7.4	14
Lanthanum	9.5	6.5	5.1	9.4

Source: Zubovic 1975. (From Davis and Boegly 1978).

Table 2. Distribution of Environmentally Hazardous
Trace Elements (ppm in coal)

Element	Region			
	Powder River Basin	Western Interior	Eastern Interior	Appalachian
Antimony	0.67	3.5	1.3	1.2
Arsenic	3	16	14	18
Beryllium	0.7	2	1.8	2.0
Cadmium	2.1	20	2.3	0.2
Mercury	0.1	0.13	0.19	0.16
Lead	7.2		34	12
Selenium	0.73	5.7	2.5	15.1
Zinc	33		250	13

Source: Zubovic 1975. (From Davis and Boegly 1978).

Oxygen Concentration

As long as there are significant amounts of oxygen, reactions (1), (2), and (3) will go to completion. In oxygen limited environments such as the interior of a tightly compacted coal pile and in coal slurry pipelines, these reactions may be limited by a lack of oxygen. As a result, the amount of acidity produced will decrease causing lower concentrations of heavy metals and trace elements and a higher pH in the leachate. Wewerka observed this trend in his batch leaching studies of an Illinois coal.³⁷ Metry, however, did not observe this effect in a column leaching study conducted with a western coal.³³ The leachate from the anaerobic column had higher concentrations of total dissolved solids (TDS) and alkalinity, and approximately the same concentration of heavy metals and trace elements when compared with the leachate from the aerobic column. This could occur if there is a sufficient amount of oxygen present in the leaching water to react with the pyrite sulfur in the coal and produce normal amounts of acidity.

Particle Size

The size of the coal particles has a pronounced effect on the inorganic quality of the leachate. Experiments conducted by Wewerka, et al. and Boegly, et al., revealed that coal samples containing smaller particle sizes produced leachates with higher metal concentrations.^{34,37} This is due to the increased surface area for the chemical reactions involved in the leaching process to occur which enhances the leaching of metals and trace elements present in coal. Boegly's study involved column leaching tests while Wewerka's study involved batch leaching tests.

Reaction Time

Another factor that affects leachate quality is the amount of contact time the coal has with water. Longer contact time results in higher metal and trace element concentrations. Anderson and Youngstrom observed this effect in their study of coal pile drainage.³⁸ Wewerka observed this effect in batch leaching studies.³⁷

Weeter, et al. observed in column studies that longer control time increased the soluble TOC concentration in the leachate from Wyodak coal.³⁹ However, the soluble TOC concentration was not influenced by contact time for an East Tennessee blend coal leachate.

In batch studies, Weeter, et al. observed that the soluble TOC concentrations reached their peak after 24 hours and then remained constant for a period of 30 days for both coals.

Percentage of Coal in Slurry

The effects of the percentage of coal in coal slurries on the leachate quality was investigated by Godwin and Manahan.⁴⁰ They found that in general COD and metal concentrations in the leachate increased with increases in the percentage of coal in the slurry. In 2% slurries, humic matter leaches from the coal and makes the primary contribution to COD. As the percentage of coal increases, the humic matter is reabsorbed and other lower weight organic compounds make up the major contribution to COD.

Three types of leaching behavior were observed with the metal ion concentrations (Figures 5 A, B, and C). Type 1 behavior is represented by sodium ion. The Na^+ concentration increased linearly with an increase

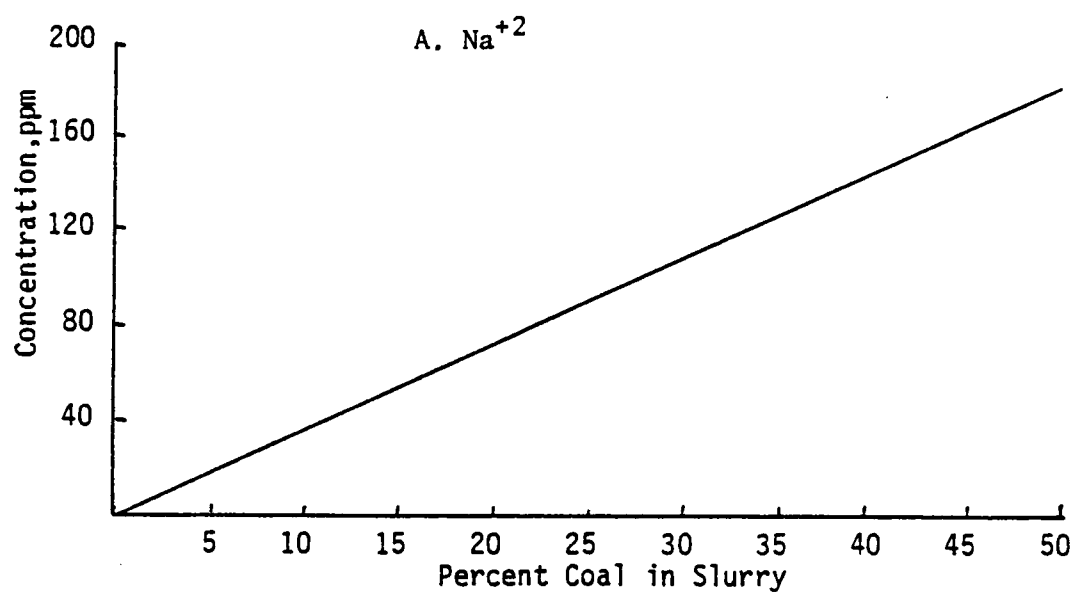


Figure 5. Leaching behavior of metal ions.

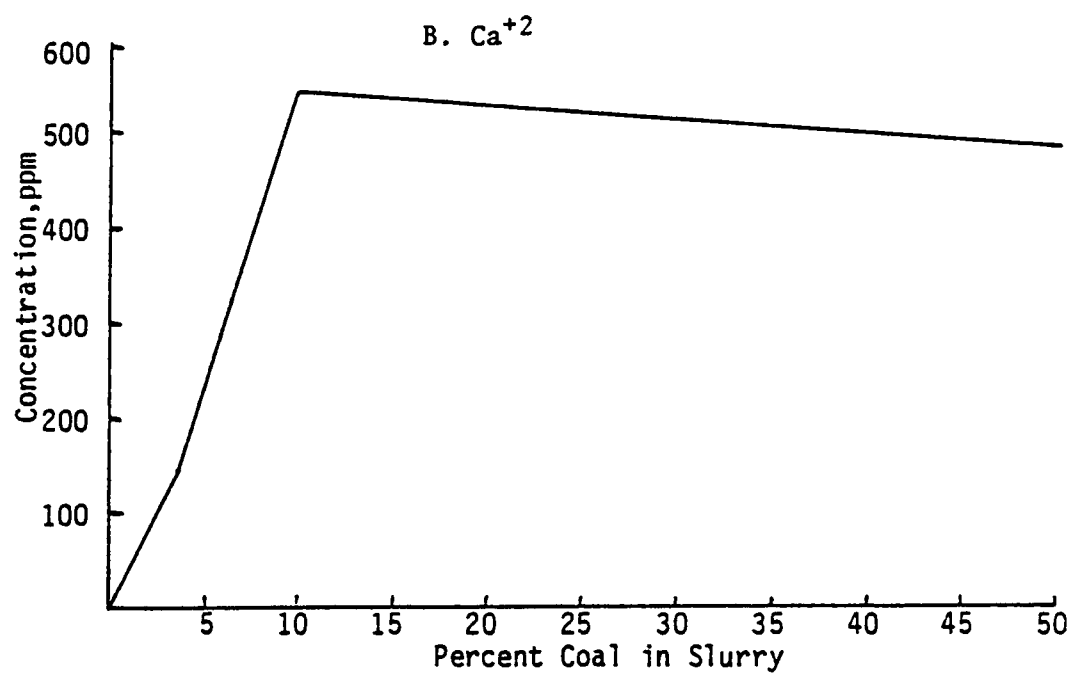


Figure 5. (Continued)

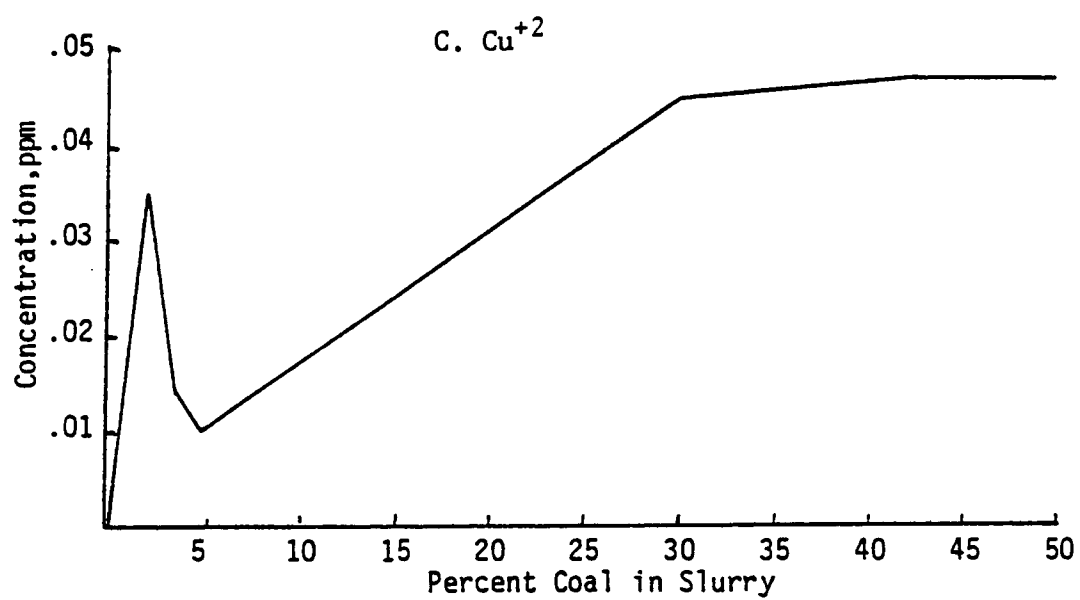


Figure 5. (Continued)

in the percentage of coal in the slurry. This indicates that the solubility limit was not reached. Type 2 behavior is represented by Ca^{+2} . The Ca^{+2} increased as the percentage of coal increased until 10% coal in slurry where it leveled off to a fairly constant value. This type of behavior indicates the solubility product of Ca^{+2} was reached. Type 3 behavior is represented by Cu^{+2} . A sharp increase in its concentration at the 2% coal in slurry indicates the formation of soluble metal humates. As the percentage of coal in the slurry increases, the humates are reabsorbed causing a decrease in Cu^{+2} concentration. From the 5% coal in slurry on, Cu^{+2} behaves like a type 2 metal. Type 1 metals were lithium, sodium, and magnesium; type 2 metals were potassium, manganese, calcium, and zinc; and type 3 metals were iron, copper, and aluminum.

D. Coal Structure

The exact chemical structure of coal is unknown, however, previous research has found that (1) coal consists of an aromatic-aliphatic structure with only three to five aromatic rings per lamella, (2) these aromatic ring clusters are joined together by four types of bridges: (a) short aliphatic group, principally methylene: generally less than four carbons; (b) ether linkages; (c) sulfide and disulfide; and (d) biphenyl types, (3) sulfur and nitrogen are incorporated into heterocyclic rings, and (4) oxygen exists mainly as hydroxyl and carbonyl groups.^{41,42}

The most reactive sites in the coal molecule are probably at the bridges connecting aromatic groups. Bond cleavage at these sites would result in the formation of heteroatom (oxygen, nitrogen, sulfur) containing aromatic compounds consisting of one to five aromatic rings. Other possible reactive sites are at the bonds connecting aliphatic

functional groups to an aromatic ring. Bond cleavage at this location would produce short (<6 carbons) aliphatic compounds containing nitrogen, sulfur, or oxygen atoms.

The only organic compounds that have been identified in coal leachate are phenols.³² Featherby and Dodd reported a phenols concentration of 1-12 ppb in the leachate from a coal pile, while Weeter, et al. reported a phenol concentration of 14 ppb.³⁹

Carlson, Weeter, and Wewerka conducted high pressure liquid chromatography and gas chromatography analysis on coal pile leachates but their works were inconclusive as to the identity of the organic compounds present. Figures 6 and 7 show some representative chromatographs obtained in Carlson's and Wewerka's work.^{37,39,43}

E. Characteristics of Coal Leachate

Tables 3-6 are compilations of data pertaining to coal pile and coal slurry leachates. It is difficult to compare results from these studies due to differences in analytical conditions and techniques and a lack of information regarding these conditions and techniques. However, these tables do show general magnitudes of parameters monitored in coal leachates. It can be seen from these tables that most of these studies have concentrated on the inorganic quality of coal leachate. The only organic parameters monitored were BOD, COD, TOC, and phenols. Wewerka, et al., Weeter, et al., and Carlson, et al., analyzed for organic compounds using high pressure liquid chromatography and gas chromatography but their studies were inconclusive in the identification and quantification of the organics present in the leachate.^{37,39,43}

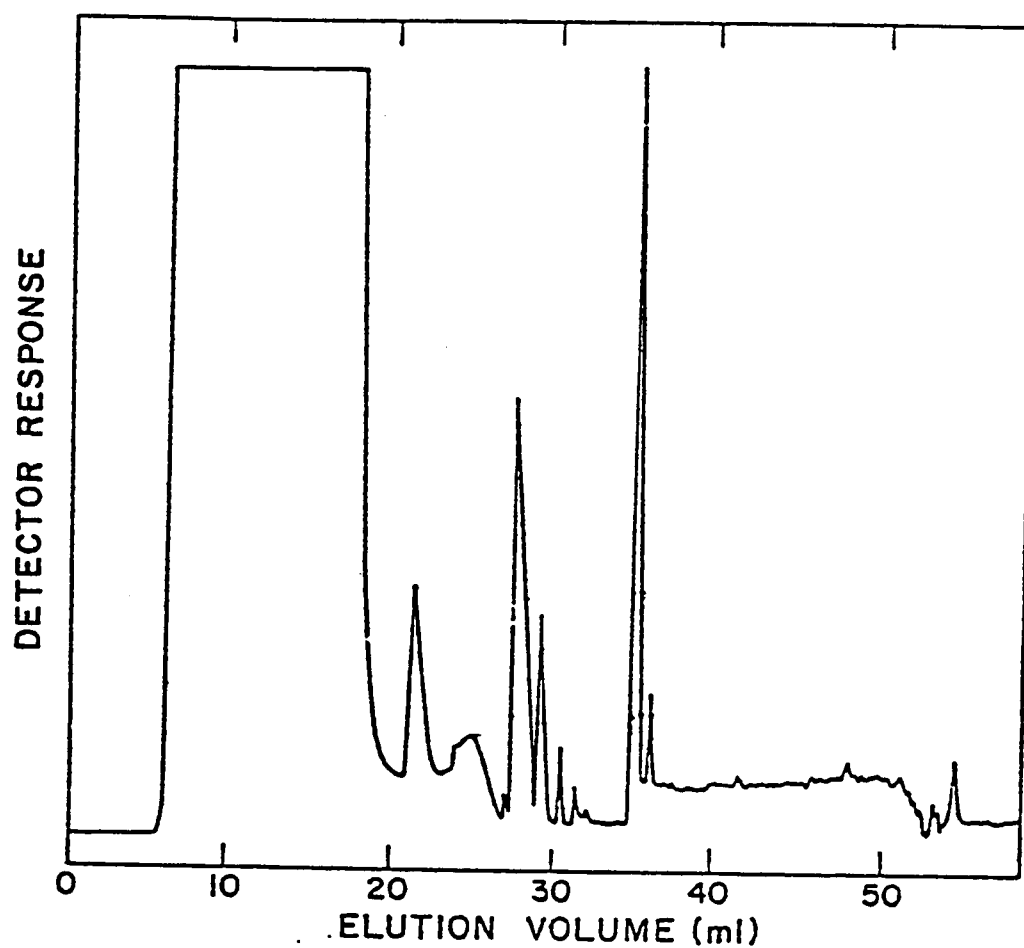


Figure 6. Liquid chromatogram of organic constituents in coal leachate.

Source: Wewerka, E.M., et al., "Trace Element Characterization of Coal Wastes," - Second Annual Report, DOE LA-7360-PA, July 1978.

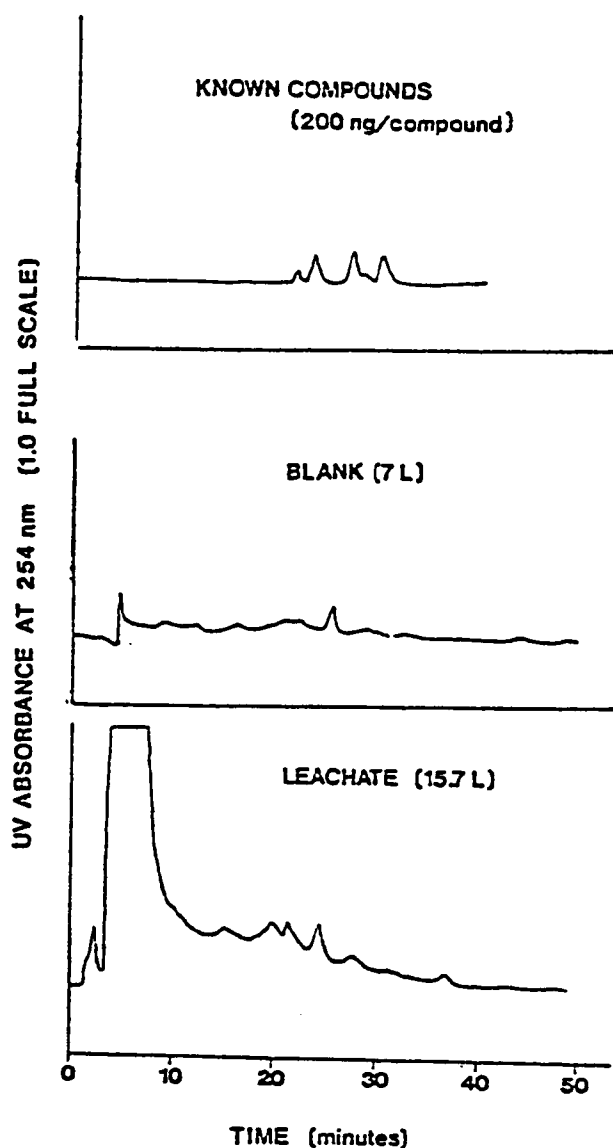


Figure 7. Purified water leachate (centrifuged) liquid chromatogram.

Source: Carlson, R.M., et al., "Implications to the Aquatic Environment of Polynuclear Aromatic Hydrocarbons Liberated from Northern Great Plains Coal," Paper Received from Robert M. Carlson, Environmental Research Laboratory, Duluth, Minnesota.

Table 3. Inorganic Constituents of Eastern Coals (in ppm)

Parameter	[*] a	^{**} b	[*] c	[*] d	[*] e	[*] f	[*] g	^{***} h
pH	2.36-3.37	6.28-7.62	2.4-2.9	2.3-3.1	2.2-5.8	2.1-3.0	2.9	1.9-5.4
TSS	200-13,000	2521-1264		8-2300			550-810	.1-58
TSD	600-115,000	259-1136	4600-11,600	2500-16,000	9332-14,948	720-44,050	1500-3200	
Alkalinity	300-4600							
Acidity			300-2850	300-7100	375-8230		270-1700	
Iron	18-1400	3.1-9.1	150-1000	62-1800	10-5250	.17-93,000	510-830	
Sulfate	380-600	66-648	1100-6900	870-9600		525-21,920	2600	
Nitrate		.12-.33						
K			1.6-10				.5	
Al	18-400		48-75	22-440			.190	
Mn	3.75-15	.03-.44	3-412	.88-45	4.5-72		27-110	
Sb	2.1-7.5	.005-.01						
As		4.1-23	.02-.1	.005-.6			.009-.01	
Be			<1	.01-.07			<.01	

Table 3 (Con't)

Parameter	[*] a	^{**} b	[*] c	[*] d	[*] e	[*] f	[*] g	^{***} h
Cd			.002	.001-.003			.001-.006	
Cr			.02-.4	.005-.011	.1-7.5	15	<.005	
Cu		.02	.2-1.6	.01-.46	.1-6.1	1.6-3.4	510-83	
Pb		.05-.06	.2				<.01-.023	
Ni		.06-.09	.2-2.8	.24-4.5			.32-1.7	
Se	12.5-23.8		.005-.02	.001-.03			.03-.003	
Ag								
Hg		.001		.0002-.007				
Th								
Zn	.008-.14		.2-.3	1.1-16	2.4-26	1.6-23		
Cl	.33		110-440					
Cn	.001-.002							

Table 3 (Con't)

Parameter	^a	^{aa} b	^a c	^a d	^a e	^a f	^a g	^{aaa} h
Co			.09-.4					
V			<1					
Mo			<1					
Ca			200-540				240-350	
Mg			9-447				.023-1.2	
Na			140-440				4.1	

NOTES:

a = Brookman, Binders and Wade^{42,44}b = Wachter³c = Featherby and Dodd 1977³²

Table 3 (Con't)

d = Cox, Chu and Ruane 1977^{43,45}e = Anderson and Youngstrom 1976³⁸f = Nichols 1974⁴⁵g = Chu, Ruane and Steiner 1976^{44,47}h = Weeter, et al., 1979³⁹

* = Field Studies

** = Laboratory Studies

*** = Field and Laboratory Studies

Table 4. Organic Constituents of Eastern Coals (in ppm)

Parameters	a*	b**	c*	d**	e***
TOC		251-373.2	37-161	5-50	2-19
COD		1407-1556			
BOD		<5			
Phenols			.012-.001		0.014

a = Brookman, Binder, and Wade^{42,44}

b = Wachter³

c = Featherby and Dodd, 1977³²

d = Wewerka, et al., 1978³⁷

e = Weeter, et al., 1979³⁹

* = Field Studies

** = Laboratory Study

*** = Field and laboratory studies

Table 5. Inorganic Constituents of Western Coal (in ppm)

Parameter	a ^{**}	b ^{**}	c [*]	d ^{**}	e ^{**}	f ^{***}
pH	2.81-7.24			7.0-8.0	4.34-4.96	6.2-6.6
TSS	1553-2486	40				
TDS	1900-5539	490-1720				
Sulfate	240-4820			34.6-189	189	
Fe	8.2-1131	.65-12		<1.0	.5	.3-.6
Mn	.4-17.9	<.05-.08			53	
Nitrate	.09-1.8					
Sb	10.3-14.0		3.5			
As	5.6-10.1		16			
Be			2			
Cd	.005-.05	<.05	20			
Cr	.03-.04	<.05			14-16	
Cu	2.2	.1-.15			42-46	
Pb	107-.33	<.1			41-65	
Ni	.05-10.2				3.8-13.8	
Se	15.0-25.2		5.7			
K					.044	
Zn	.15-25.0	.15-.23			44-53	
Hg	.004-.005		.13			
Al					1.3	
Cl	2.3					

Table 5 (con't)

Parameter	a ^{**}	b ^{**}	c [*]	d ^{**}	e ^{**}	f ^{***}
Cn	22.5					
V		<2				
Sr		.2-.33				
Li		2.05			6.0-6.4	
Ca					1.1	
Mg					.21	
Na					.057	
Co						
Alkalinity	3	37.5-124				

a = Wachter³b = Metry, 1975³³c = Zubovic, 1975³⁶d = Boegly, 1978³⁴e = Godwin and Manahan, 1979⁴⁰f = Weeter et al, 1979³⁹

* = Field Study

** = Laboratory Study

*** = Field and Laboratory Studies

Table 6. Organic Constituents in Western Coal (in ppm)

Parameter	^{**} a	^{**} b	^{***} c
COD	80-300	1053-1826	
BOD		<1.2-F2.5	
TOC		90-318.4	24-78

a = Godwin and Manahan, 1979⁴⁰

b = Wachter³

c = Weeter, et al.³⁹

** = Laboratory Study

*** = Field and Laboratory Studies

Eastern Coal Leachate

In general this leachate has a pH between 2.0 and 3.0 although Wachter and Anderson and Youngstrom reported pH values as high as 7.62 and 5.8 respectively.^{3,38} Other investigators have observed the following ranges for parameters monitored in the leachates; total suspended solids (TSS): 200-13000 ppm; total dissolved solids: 600-115,000 ppm; alkalinity: 300-4600 ppm; acidity: 300-2850 ppm; iron: 3.1-93,000 ppm; and sulfate: 66-21,920 ppm. The heavy metals and trace elements usually had concentrations less than 1.0 ppm although Cu, Al, Cl, Ca, Mn, Mg, and Na had concentrations between 100 and 500 ppm. The ranges observed for the organic parameters monitored in the leachate were; TOC: 5-373.2 ppm; COD: 1407-1556 ppm; BOD: <5.0 ppm; and phenols: 1-12 ppb.

Western Coal Leachate

Reported values for western coal leachates are as follows; pH: 2.81-8.0; TSS: 40-2486 ppm; TDS: 490-5539 ppm; iron: 0.30-1131 ppm; and sulfate: 34.6-4860 ppm. Most of the metals and trace elements have concentrations less than 1.0 ppm although Cd, Cr, Cu, Pb, Na, Se, Zn, and Cn have concentrations between 10-65 ppm. COD values range from 80-1826 ppm; BOD: <1.2 to <2.5 ppm; and TOC: 90-318.4 ppm.

In comparing the Eastern coal leachate with Western coal leachate, the Eastern coal leachate generally had a lower pH and higher concentration of TSS, TDS, iron, and sulfate. The TOC and COD values were approximately the same although the lowest and highest values were reported from an Eastern coal leachate. The BOD for Western coal leachate was approximately the same as the Eastern coal leachate.

The trace element and metal concentration as a whole were higher in the Eastern coal leachate than in the Western coal leachate although higher concentrations of Cd, Cr, Cu, Pb, Na, Se, Zn, and Cn were observed in leachate from Western coal.

F. Summary

1) Oxidation of FeS_2 initiates the leaching of heavy metals, trace elements, and organic compounds from coal.

2) In bicarbonate buffered solutions the rate law is:

$$\frac{-d[\text{Fe(II)}]}{dt} = k [\text{Fe}^{+2}] [\text{OH}]^2 p_{\text{O}_2}$$

3) In bicarbonate buffered solutions with iron concentrations from 1-50 ppm the rate law is:

$$\frac{-d[\text{Fe(II)}]}{dt} = k [\text{Fe}^{+2}] [\text{OH}]^2 [\text{Alk}]^{-.75}$$

4) Copper concentrations as low as 24 ppb catalyze the reaction.

5) Sulfate concentrations do not influence the rate.

6) Hydroxylate aromatic compounds stabilize ferrous iron.

7) High sulfur eastern coals produce a leachate containing higher concentration of metals and trace elements than Western coals.

8) Lack of oxygen may limit the oxidation of FeS_2 and thus decrease the leaching of metals and trace elements.

9) Decreasing the particle size of coal increases the concentrations of metals and trace elements in the leachate.

10) Longer contact time between coal and water increase the concentrations of metals and trace elements in the leachate.

- 11) Increasing the percentage of coal in slurry increases the concentrations of metals and trace elements and COD in the leachate.
- 12) The structure of coal is unknown, however it is believed that (a) coal consists of an aromatic-aliphatic structure with 3-5 aromatic rings per lamella, (b) these ring clusters are joined together by four types of bridges: (1) short aliphatic groups; (2) ether linkages; (3) sulfide and disulfide; and (4) biphenyl type, (c) sulfur and nitrogen are incorporated into heterocyclic rings, and (d) oxygen exists mainly as hydroxyl and carbonyl groups.
- 13) Eastern coal leachate generally has a lower pH and higher metal and trace element concentrations, TSS, TDS, and sulfate concentrations in comparison to western coal leachate.
- 14) The TOC, COD, and BOD concentrations were approximately the same in both western and eastern coal leachates.

III. EXPERIMENTAL DESIGN

A. Experimental Matrix

A two way classification analysis of variance (ANOVA) with fixed effects was used to determine whether or not coal particle size and the percentage of coal in slurry significantly affected the leaching of organic compounds from Wyodak coal.

Three particle size distributions (1, 2, and 3) and four coal slurry mixtures (A, B, C, and D) were used in this study giving a total of 12 particle size distributions - coal slurry combinations per experimental run. Four replicate runs were conducted giving a total of 48 observations for the entire experiment.

The three size distributions were obtained by passing coal through various sieves; size distribution 1 consisted of coal passed through a 2.00 mm sieve and retained on a 0.500 mm sieve; distribution 2 consisted of coal passed through the 0.500 mm sieve and retained by a 0.250 mm sieve; and size distribution 3 consisted of coal crushed with a ball mill and passed through a 0.074 mm sieve.

The four coal slurry mixtures were obtained by varying the amount of coal and water added to a 500 ml Erlenmeyer flask. The follow slurries were used in this study; A: 6.25% coal; B: 12.50% coal; C: 25.0% coal; and D: 50.0% coal. Slurries A, B, and C were made with 400 ml of deionized water while ratio D was made with only 100 ml of water due to volume limitations of the 500 ml Erlenmeyer flask.

After the coal and water were added to the flasks, oxygen was purged from the flasks with nitrogen gas. The flasks were then sealed

with a teflon screwcap. Each sample was shaken for 24 hours at a temperature of 22°C. The samples were then allowed to sit for 24 hours before analysis to facilitate the filtration of the sample.

Experiment Modifications

All four slurries were used with particle size distributions 1 and 2, however, only slurries A and B were used with size distribution 3. At this size distribution, the coal absorbed essentially all of the water in slurries consisting of 25% and 50% coal leaving no leachate for analysis. Since slurry D was composed of 100 ml of water and 100 grams of coal, 250 ml of leachate could not be collected for extraction and concentration of the organic compounds. Only 50 ml of leachate were collected for the extraction and concentration procedures.

B. Sample Preparation

The leachate from the flasks was filtered through a Whatman GF/C filter which has an effective particle retention size of 1.2 microns (μ). After filtration the initial nonvolatile TOC (INVTOC) and pH were taken. The pH was increased to 11.0 with NaOH to precipitate ferrous iron as ferrous hydroxide and filtered through a Whatman GF/C filter. After filtration, the pH was adjusted to 7.0 with HCl and the extraction nonvolatile TOC (EXNVTOC) was taken. At this point the leachate was ready for the extraction and concentration of the organic compounds present.

C. Adsorption, Concentration, and Elution of Organic Compounds

Two hundred and fifty milliliters of the leachate was gravity fed through a Waters C18 Sep Pak at a rate of approximately 0.5 ml/minute to extract and concentrate any organics present in the leachate. Figure 8 illustrates the extraction apparatus. Those organics retained by the Sep Pak were then eluted with 2.0 ml of acetonitrile. This eluate was then spiked with 2-naphthol which was used as the internal standard. After spiking the sample, the eluate was ready for analysis using high performance liquid chromatography (HPLC).

D. HPLC Analysis of the Eluate

Isolation and partial separation of the organic compounds in the acetonitrile eluate were accomplished using reverse-phase, gradient elution liquid chromatography. A Spectra Physics 3500B Chromatograph and a Schoeffel SF770 Ultraviolet detector were used in this analysis. The following conditions were used for the analysis of these samples:

Instrument:	Spectra Physics 3500B
Column:	Waters C18
Flow Rate:	1.0 ml/min.
Gradient:	100% H ₂ O for 10 minutes: increased linearly to 99% acetonitrile over a period of 20 minutes
Injection Volume:	10 µl
Detector:	Schoeffel SF770 Ultraviolet Detector
Wavelength:	280 nanometers
Absorbance:	0.4

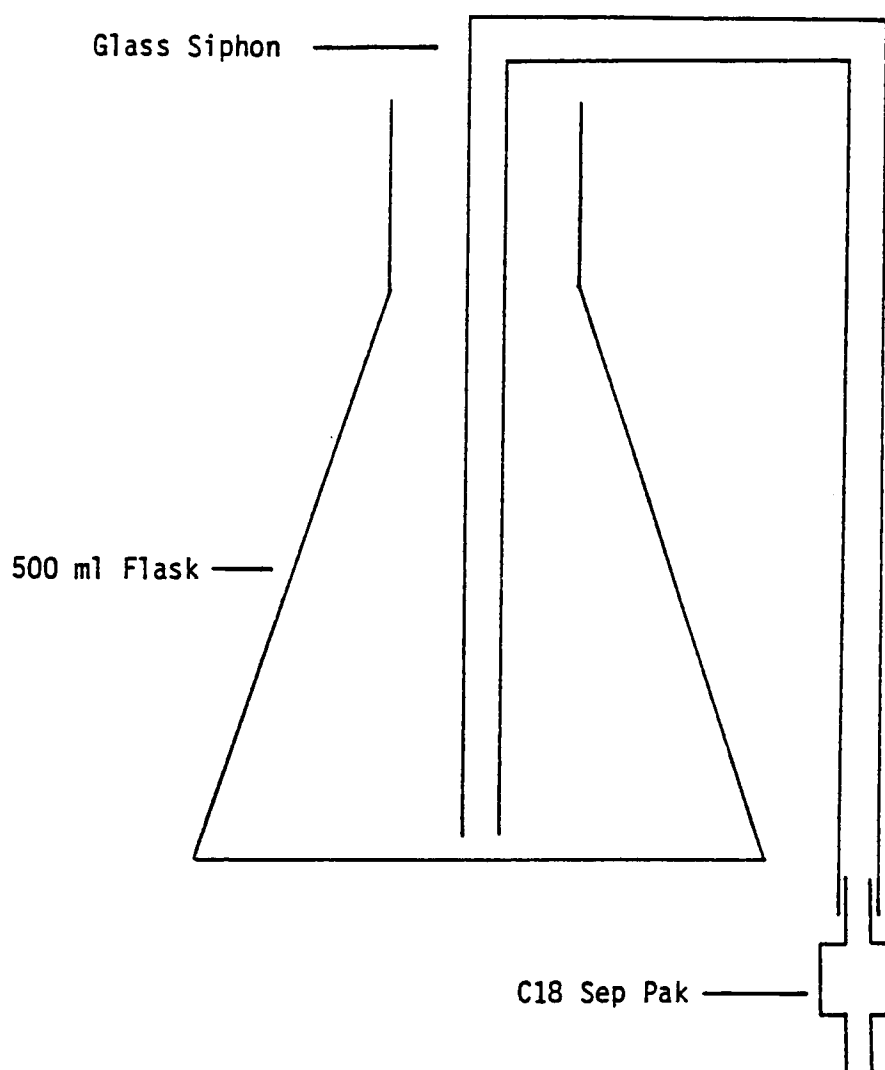


Figure 8. Extraction apparatus.

Ten microliters of the eluate was injected onto the C18 column. One hundred percent water was run through the column for 10 minutes. After 10 minutes, a linear gradient was run which increased the concentration of acetonitrile from 0 to 99% over a period of 20 minutes. The solvent was held at 99% acetonitrile until the organic compounds have eluted from the column. The eluted organics were then detected with the Schoeffel SF770 Ultraviolet Detector.

E. HPLC Analysis of Phenols

Four phenols, catechol, vanillin, phenol, and 8-quinolinol were separated using reverse-phase, gradient elution chromatography. A Spectra-Physics 3500B Chromatograph, Schoeffel SF 770 Ultraviolet detector, and a Waters C18 HPLC column were used for this analysis. The conditions for this analysis were the same as those conditions used in the HPLC analysis of the acetonitrile eluate in Section D.

F. Surface Area of Coal Samples

The surface areas of coal samples consisting of the three different particle size distributions were used to explain any significance of coal particle size on the leaching of organic compounds from Wyodak coal. Two methods were used to determine the surface area; method one measured the surface area of the sample with a Micromeritics BET Surface Area Analyzer; method two calculated the surface area with the $\log d_{32}$ equation.

BET Surface Area

The surface area of powdered or solid porous materials is measured with the Surface Area Analyzer by determining the quantity of gas necessary to form a single layer of gas molecules on a representative sample. Testing is accomplished using nitrogen gas at the temperature of liquid nitrogen because, under these conditions, the gas molecules are adsorbed on the solid surface. The space occupied by each adsorbed molecule is known within relatively narrow limits under this condition.

One form of the BET equation that describes the adsorption of a gas on a solid surface is

$$\frac{p/p_s}{v[1-(p/p_s)]} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C} \right] \frac{p}{p_s} \quad (1)$$

where V is the volume (at standard temperature and pressure) of gas adsorbed at pressure p , p_s the saturation pressure, V_m the volume of gas required to form an adsorbed monomolecular layer, and C a constant related to the energy of adsorption. When experimental data are plotted as $(p/p_s) \div V[1-(p/p_s)]$ on the ordinate against p/p_s as the abscissa, a straight line results for p/p_s values between about 0.05 and 0.35, the intercept and the slope of which are, respectively, $1/V_m C$ and $(C-1)/V_m C$. Since C is a comparatively large number, $C-1=C$. The monolayer volume V_m is thus expressed as the reciprocal of slope plus the intercept.

The surface area of the adsorbing sample is calculated from the monolayer covering gas volume V_m , the area covered by a single gas molecule, Avagadro's number giving the total number of gas molecules in a mole of gas at standard temperature and pressure, and the molar volume of the gas. Using 16.2Å^2 as the area covered by an adsorbed nitrogen

molecule according to the latest critical evaluation⁴⁸, the relationship giving the sample surface area S becomes

$$S = \frac{4.35}{(\text{slope} + \text{intercept})} \quad (2)$$

Sample Analysis

Approximately four grams of coal consisting of either size distribution 1, 2, or 3 were degassed at 105°C for approximately 40 minutes to remove any moisture in the sample. The total surface area for the sample was then determined using nitrogen gas and liquid nitrogen on the Micromeritics BET Surface Area Analyzer which determined the surface area in square meters. By dividing the total surface area by the weight of the sample (in grams) the surface area per gram is determined for the sample.

Log d_{32} Surface Area Calculation

The surface area was also determined using the equation

$$\log d_{32} = \log M'_g - 1.1513 \log^2 \sigma'_g \quad (3)$$

where $\log d_{32}$ is the volume per unit area (V/A), M'_g is the mass mean diameter, and σ'_g is the geometric standard deviation. The mass mean diameter and σ'_g were determined through sieve analysis for particle size distributions 1 and 2 while the Coulter Counter was used to determine these parameters for particle size distribution 3.

The parameters M'_g and σ'_g were determined for size distributions 1 and 2 by sieving a representative of each sample through a set of calibrated sieves. Size distribution 1 particles were sieved through sieve openings ranging from 2.00 mm to 0.420 mm while size distribution 2 was sieved through openings ranging from 0.590 mm to 0.177 mm.

Starting with the weight of screenings shaken downward through the vertical stack of successively finer sieves to the bottom pan, the portions of coal held between adjacent sieves are added in sequence and the cumulative weights are recorded. After conversion into percentages by weight equal to or less than the rated size of the overlaying sieve, a summation curve can be plotted on log probability paper plotting cumulative weight percentage versus sieve openings (particle diameter).

M'_g , d_{16} , and d_{84} can be obtained from this graph. M'_g is the particle diameter at 50 cumulative weight percent, d_{16} is the diameter at 16% and d_{84} is the diameter at 84%.

The geometric standard deviation is then calculated from the following equation:

$$\sigma'_g = (d_{16}/M'_g + M'_g/d_{84})/2 \quad (4)$$

M'_g , d_{16} , and d_{84} were determined for size distribution 3 using the Coulter Counter. This instrument determines the number and sizes of particles suspended in a conductive liquid (5% LiCl in methanol) by forcing the suspension to flow through a small aperture and monitoring an electrical current which also passes through the aperture. Electrodes are immersed in the conductive fluid on opposite sides of the aperture. As a particle passes through the aperture, it changes the resistance between electrodes. This produces a current pulse of short duration having a magnitude proportional to the particle volume. The series of pulses are electronically scaled and counted. It should be noted that since volume equals weight divided by density, relative volume and relative weight curves are identical assuming constant density for all particles in the system. After the instrument produces the

cumulative weight percent versus particle diameter plot, M'_g , d_{16} , d_{84} , and σ'_g can be determined as in the sieve analysis. Once these parameters are known, the volume per unit area can be calculated by equation (3). The specific surface area (m^2/g) can then be calculated by multiplying the volume per unit area by the sample density and taking the reciprocal of the product.⁴⁹

The density of the samples was determined by a Micromeritics Helium Pycnometer. This instrument operates on the principle that the change in the pressure of a nonadsorbing pure gas, in this case helium, within an enclosed vessel accompanying a discrete change in the volume of the vessel is a function of the volume of any solid object also in the vessel. The volume of the object can be established from the functional relationship, and the density (g/cc) of the object is then directly obtained by dividing its weight, as determined separately by its volume.⁵⁰

G. Extraction Efficiency of C18 Resin, XAD-2 Resin, Tenax GC Resin, and Activated Charcoal

The extraction efficiencies of these adsorbents were determined by measuring the NVTOC levels of the leachate before (extraction NVTOC) and after (eluate NVTOC) the leachate passed through the adsorbents. The efficiencies were then determined by the following equation.

$$[(\text{extraction NVTOC} - \text{eluate NVTOC}) / \text{extraction NVTOC}] \times 100$$

The C18 resin was contained in prepacked cartridges 1.3 cm in length and 1.3 cm in width. The other adsorbents were packed into disposable glass pipettes resulting in a bed depth 15 cm in length and 1 cm in width.

Two hundred and fifty milliliters of leachate with an extraction TOC of 30 ppm, were passed through the packed columns at a rate of approximately 0.5 ml/min. The C18 Sep Paks were tested over a larger range of extraction TOC levels (26-362.0 ppm) since they were used to extract and concentrate the organics in this study. An overall extraction efficiency was determined as well as an average extraction efficiency for leachates whose TOC levels were approximately 30 ppm (26.0, 27.0, 30.5, and 33.5 ppm).

H. Molecular Weight Analyses

The molecular weight distribution of the leachate was analyzed on a Sephadex K25/100 column packed with Sephadex G-25 superfine gel. This gel is a bead formed gel prepared by cross-linking dextran with epichlorohydrin.⁵¹ The column was fitted with upward flow adaptors and was packed with the gel to a bed depth of 70 cm. The width of the column was 2.5 cm which gave a total bed volume of 344 ml.

The eluate was a buffer solution 0.10 molar in NaH_2PO_4 and 0.05 molar in NaOH. This solution had a pH of 7.2 and an ionic strength of 0.23 moles/liter. A flow rate of 0.5 ml/min was used for the analyses.

The leachates analyzed were obtained using particle size 1 in a 50% coal slurry, particle size 2, also in a 50% coal slurry, and a particle size 3 in a 25% slurry. This last leachate was concentrated by vacuum distillation to increase the NVTOC level. These leachates underwent the same sample preparation of section B. Three milliliters of the leachate were injected onto the column and the column eluate was collected in 10 ml fractions with a Buchler 200 fraction collector. Each fraction was analyzed for nonvolatile total organic carbon (NVTOC) and an NVTOC profile of the eluate was obtained.

A retention coefficient, R , was calculated for fractions containing relative high NVTOC concentrations by dividing the fractions elution volume (V_e) by the void volume (V_o). The void volume is the elution volume of molecules only distributed in the mobile phase. V_o was determined with Blue Dextran 2000 which has a molecular weight of 2 million and was found to be 150 ml for this column. These retention coefficients were used to provide a profile of the relative molecular weights of the organic compounds present in the leachate. Low R values correspond to higher molecular weights while high R values correspond to lower molecular weights.

I. Data Analysis

Analysis of variance techniques were employed to determine if observed differences in measured responses were significant and which of the two factors, particle size distribution or percentage of coal in the slurry, were responsible for the observed differences. Significance for a particular factor was determined at the 5% level. Any significance of coal particle size was explained by either the BET surface areas or the $\log d_{32}$ surface areas of the samples.

The parameters monitored in this study were INVTOC, EXNVTOC, and the chromatographic peaks representing organic compound(s) obtained from the HPLC analysis of the acetonitrile eluate. Each peak on the chromatogram was identified according to its elution time. The response of the peak was measured according to its peak height. Each peak response was normalized by dividing its height by the peak height of the internal standard. The elution time of the peaks were also normalized by subtracting the individual peak elution time from the internal standard

elution time. These normalizations were done to account for possible variations in detector response, injection technique, and flow variations.

J. Preliminary Research

It should be noted that preliminary research was conducted to determine what type of coal to use in this study, the method for extracting and concentrating the organic compounds present in the leachate, and the method of analyses to isolate and partially separate the extracted compounds.

Wyodak coal was chosen over Illinois #6 coal because its leachate contained organic compounds in sufficient concentrations which could be extracted and analyzed using high performance liquid chromatography.

The C18 Sep Paks were used to extract and concentrate the organics present in the leachate because the compounds eluted from the Sep Paks could be isolated and partially separated using HPLC. The organic compounds present in the leachate were also extracted with an organic solvent (either methylene chloride or hexane). However, the organics extracted by these solvents could not be separated using HPLC. Therefore, this method was not used.

Isolation and partial separation of the organic compounds extracted by both of the above methods were attempted using flame ionization gas chromatography (FID-GC). However, the FID detector did not detect the presence of any organic compounds. This could have been due to the compounds being nonvolatile or the compounds being irreversibly adsorbed to the capillary column (OV-101 wall coated column). The organic compounds were methylated using diazomethane to increase their volatility

and also to prevent irreversible adsorption to the column, however, this did not help in the FID-GC analysis of the compounds.

IV. RESULTS AND DISCUSSION

A. pH, Initial and Extraction NVTOC Results

Table 7 presents the pH, INVTOC, and EXNVTOC of the leachate taken during this study. The pH of the leachate ranged from 5.3 to 6.4 and had an average of 5.7. This pH is moderately acidic which is not uncommon in western coals. The INVTOC of the leachate ranged from a low of 40 ppm to a high of 387 ppm while the EXNVTOC ranged from 26 ppm to 362 ppm. The lower EXNVTOC values were due to the coprecipitation of some of the INVTOC with ferrous hydroxide during the sample preparation.

The ANOVA results for the EXNVTOC and INVTOC data are presented in Table 8. F values greater than 2.93 indicate that the percentage of coal in the slurry significantly affects INVTOC or EXNVTOC concentrations while F values greater than 3.33 indicate that particle size distribution significantly affects INVTOC or EXNVTOC concentrations.

These results show that particle size did not significantly affect the NVTOC or EXNVTOC concentrations. This insignificance may possibly be explained by the BET surface area results. The specific surface areas for size distributions 1 and 2 ($8.9 \text{ m}^2/\text{g}$ and $8.9 \text{ m}^2/\text{g}$) were essentially the same while the specific surface area for size distribution 3 ($2.9 \text{ m}^2/\text{g}$) was only $6 \text{ m}^2/\text{g}$ less than size distributions 1 and 2. The NVTOC levels for distributions 1 and 2 should have approximately the same NVTOC levels while 3 should have lower NVTOC levels. The difference in specific surface areas may not have been large enough to cause a substantial decrease in the NVTOC concentration for size distribution 3 samples. Therefore, the NVTOC concentrations were approximately the same for all three size distributions and the effect of particle size on the INVTOC and EXNVTOC concentrations in the leachate was insignificant.

Table 7. Initial Nonvolatile Total Organic Carbon Results

Distribution Size	Coal Slurry	Experiment	pH	INVTOC, ppm	EXNVTOC, ppm
1	A	1	5.9	50.0	33.0
		2	6.0	43.0	80.5
		3	6.3	59.5	38.0
		4	5.8	46.0	38.0
1	B	1	5.8	71.0	48.0
		2	6.0	84.0	50.0
		3	5.8	72.5	58.0
		4	5.7	75.0	58.0
1	C	1	6.2	120.0	98.0
		2	5.9	120.0	120.0
		3	5.7	165.0	142.0
		4	5.7	160.0	145.0
1	D	1	5.4	330.0	262.0
		2	5.6	330.0	288.0
		3	5.6	320.0	293.0
		4	5.6	355.0	295.0
2	A	1	6.2	40.5	38.5
		2	5.7	42.0	35.0
		3	6.0	52.0	38.0
		4	4.9	45.0	36.5
2	B	1	5.6	59.5	59.5
		2	*	.	.
		3	5.9	160.0	58.0
		4	5.7	81.0	54.5
2	C	1	5.8	195.0	170.0
		2	5.5	205.0	175.0
		3	6.0	125.0	125.0
		4	5.9	150.0	137.0

Table 7 (Con't.)

Distribution Size	Coal Slurry	Experiment	pH	INVTOC, ppm	EXNVTOC, ppm
2	D	1	5.3	380.0	361.0
		2	5.4	387.0	362.0
		3	5.5	297.0	250.0
		4	5.5	265.0	245.0
3	A	1	6.0	54.5	27.0
		2	6.0	55.0	26.0
		3	6.0	49.0	37.0
		4	6.0	61.5	28.0
3	B	1	6.4	49.5	45.0
		2	6.0	60.0	42.5
		3	6.2	65.0	37.0
		4	6.1	74.0	43.0

* . = missing data

Table 8. ANOVA Results for Initial and Extraction Nonvolatile TOC

Variable	Source	F	Significance*
INVTOC	Slurry	150.07	Y
	Size Distribution	0.83	N
EXNVTOC	Slurry	176.4	Y
	Size Distribution	1.39	N

*Y = significant

N = not significant

The percentage of coal in the slurry significantly affected the INVTOC and EXNVTOC concentrations in the leachate. Figures 9 and 10 show that as the percentage of coal increased, the INVTOC and EXNVTOC concentrations increased linearly. This indicates that all of the organic matter capable of entering into solution was leached from the coal and that the leachate was not saturated with respect to these organics.

B. Surface Area Characterization and Relationship
to the Leaching of Organic Compounds

BET Surface Area Results

The surface areas measured by the BET Surface Area analyzer were 8.9, 8.8, and 2.9 m²/g for size distributions 1, 2, and 3, respectively. These results were unusual since size distributions 1 and 2 which contain the two larger particle sizes had essentially the same surface area while size distribution 3 which consists of the smallest coal particles had the smallest surface. Ordinarily the surface area for a given sample is expected to increase instead of decrease as the particle size becomes smaller. This phenomenon could occur if the coal is porous and the pore system is being reduced as the coal particles become smaller in size. Two possible causes for this reduction are; (1) the pores in the coal are being plugged by smaller particles; and (2) as the coal particle is reduced in size, it is also being compressed in such a manner as to collapse internal pores.

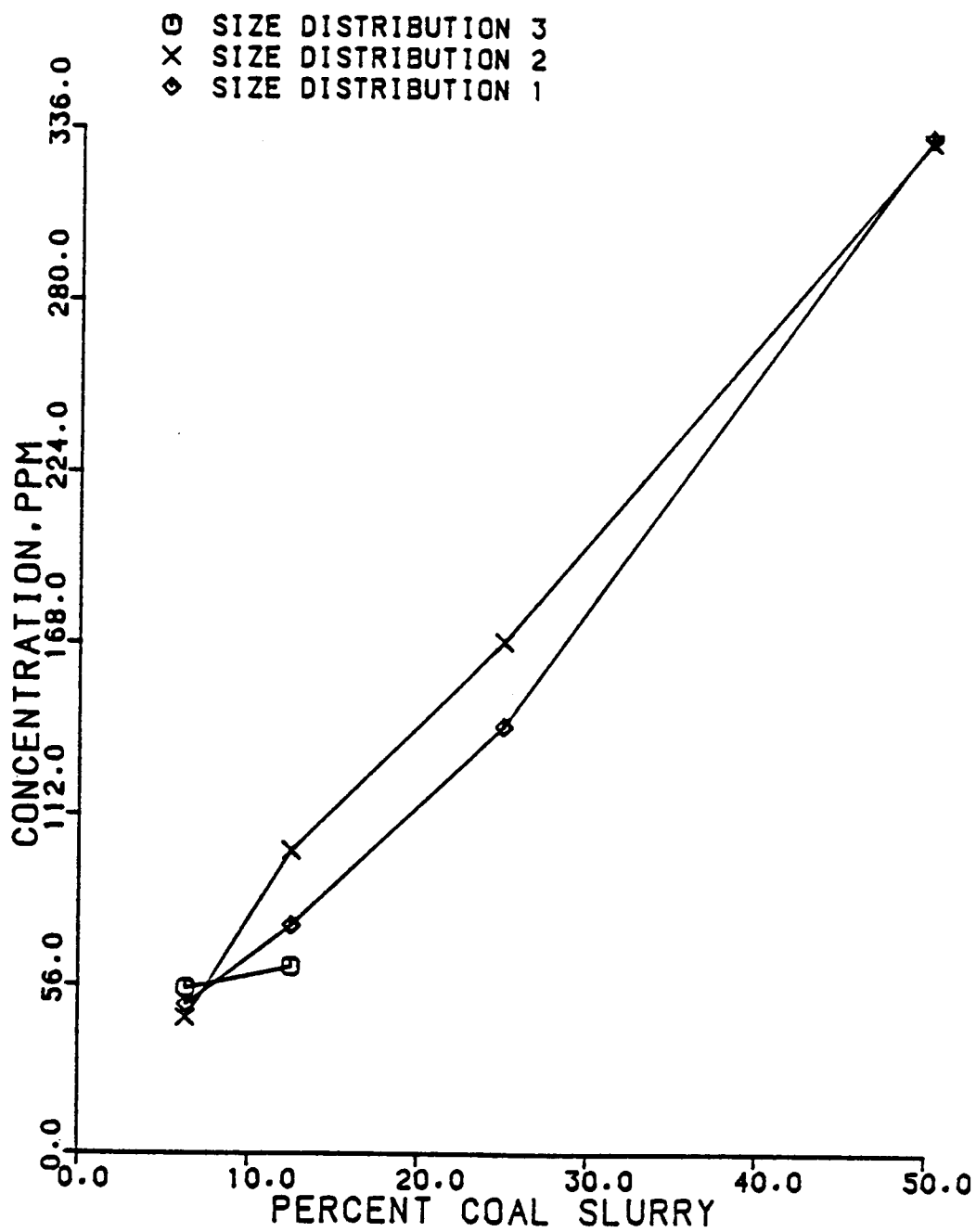


Figure 9. Influence of coal slurry on INVTOC concentration.

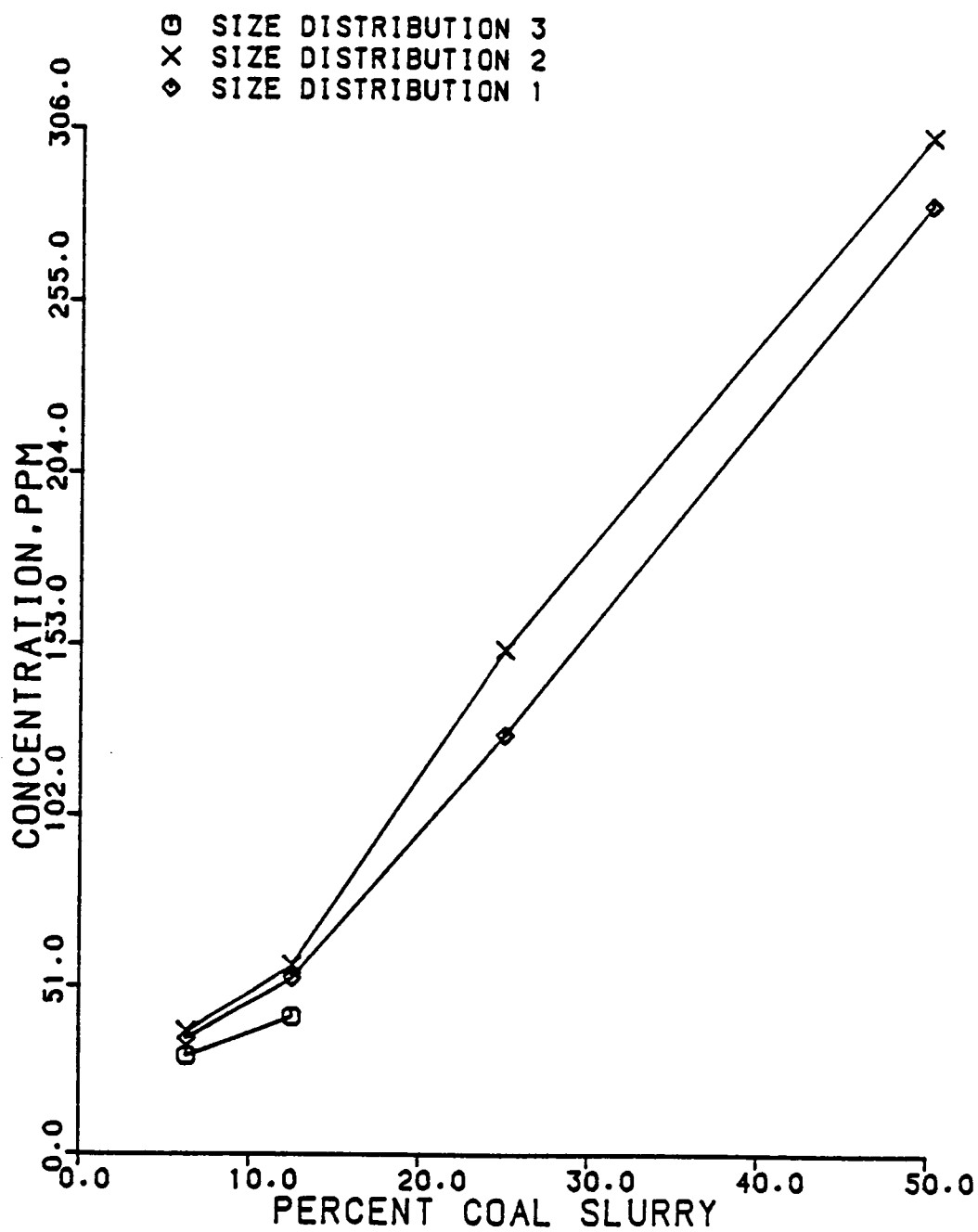


Figure 10. Influence of coal slurry on EXNVTOC concentration.

Log d₃₂ Surface Area Results

The volume per unit area (V/A) was determined using the equation

$\log d_{32} = \log M'_g - 1.1513 \log^2 \sigma'_g$ The mass mean diameter (M'_g) and the geometric standard deviation (σ'_g) used in this equation, were determined through sieve analysis for size distributions 1 and 2 and through Coulter Counter analysis for size distribution 3.

Table 9 presents the data obtained from these analyses. From these data summation curves for each size distribution were drawn which plotted the particle diameters versus the cumulative weight percent. These curves are shown in Figures 11 and 12. From these curves M'_g , d_{16} , and d_{84} were found to be; 0.820 mm, 1.44 mm, and 0.640 mm, respectively, for size distribution 1; 0.290 mm, 0.420 mm, and 0.250 mm for size distribution 2; and 0.0205 mm, 0.047 mm, and 0.008 mm for size distribution 3.

The geometric standard deviations were calculated by the equation

$\sigma'_g = (d_{16}/M'_g + M'_g/d_{84})/2$ to be 1.5, 1.3, and 2.4 for size distributions 1, 2, and 3 respectively.

Once these values were known, V/A could be calculated. For size distribution 1, V/A equaled $7.5 \times 10^{-4} \text{ m}^3/\text{m}^2$; for size distribution 2 V/A equaled $2.8 \times 10^{-4} \text{ m}^3/\text{m}^2$; and for size distribution 3, V/A equaled $1.4 \times 10^{-5} \text{ m}^3/\text{m}^2$.

In order to calculate the specific surface area, the density for each size distribution had to be known. Using the helium pycnometer, the densities for the three distributions were measured at 1.36 g/cc, 1.25 g/cc, and 1.28 g/cc for sizes 1, 2, and 3, respectively. Gan, Nandi and Walker observed densities in this range, from 1.25 to 1.67 g/cc.⁵³ The specific surface area was then calculated by multiplying V/A by the

Table 9. Sieve Analysis for Particle Size 1 and 2 Samples

Particle	Sieve Opening, mm	Weight Retained, g	Weight %	Cumulative Weight %
1	2.000	2.9	0.04	0.04
	1.680	6.9	0.09	0.13
	0.841	26.5	0.35	0.48
	0.590	34.9	0.46	0.94
	0.720	7.0	0.05	0.99
2	0.590	0.0		
	0.420	5.4	0.14	0.14
	0.256	28.1	0.71	0.85
	0.177	6.0	0.15	1.00

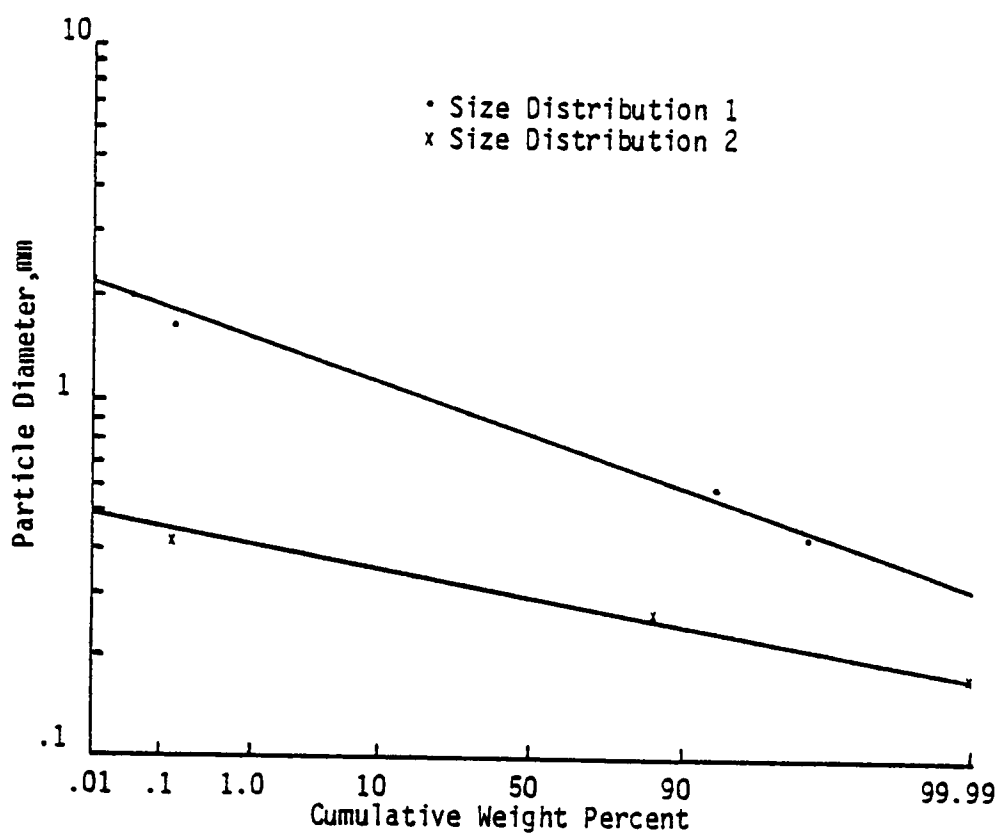


Figure 11. Summation curves for size distributions 1 and 2.

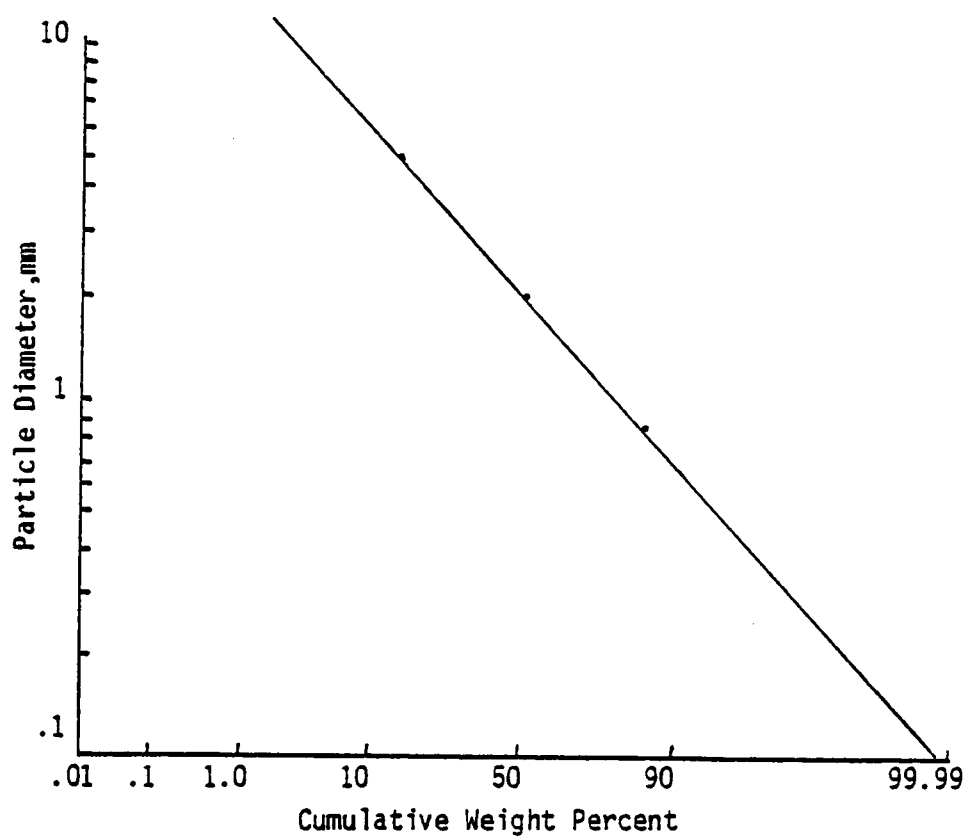


Figure 12. Summation curve for size distribution 3.

appropriate density and taking the reciprocal of the product. The specific surface areas were calculated to be $9.8 \times 10^{-4} \text{ m}^2/\text{g}$, $2.9 \times 10^{-3} \text{ m}^2/\text{g}$ and $5.6 \times 10^{-2} \text{ m}^2/\text{g}$ for distributions 1, 2, and 3, respectively.

Table 10 summarizes the results of the $\log d_{32}$ surface area calculations.

The surface area measured by the BET analyzer was approximately two to three orders of magnitude larger than that calculated by the $\log d_{32}$ method. This large difference in surface area between the two methods is the result of the pore surface area measured by the BET analyzer. The $\log d_{32}$ method treats each coal particle as a solid sphere, therefore if the pore system is extensive, the BET surface area results will be much larger. Thus the $\log d_{32}$ results support the fact that an extensive pore system is present in the Wyodak coal. Wiser mentions that as a result in the manner in which coal molecules are linked together, an extensive pore system exists in coal.⁴²

As the coal particles decrease in size, the specific surface area was expected to increase for coal samples. The results from the BET analyzer show that this was not the case for these samples. There was not much difference in the three surface areas but it was shown that size distribution 3, which had a mass mean diameter 10-40 times smaller than that of size distributions 2 and 3, had a surface area approximately 3 times smaller. Also, size distribution 2 which had a mass mean diameter about two times less than the mass mean diameter of size distribution 1, had essentially the same specific surface area as 1.

It may be difficult to ascertain the effects of surface area on the leaching of organics from coal since the access of water to these pores is unknown. Generally, as surface area increases, the leaching of

Table 10. Results of the Log d_{32} Surface Area Calculations

Size Distribution	M'_g	σ'_g	$V/A, m^3/m^2$	density, g/m^3	Specific Surface Area m^2/g
1	0.820	1.5	7.5×10^{-4}	1.36×10^6	9.3×10^{-4}
2	0.290	1.3	2.8×10^{-4}	1.25×10^6	2.9×10^{-3}
3	0.0205	2.4	1.4×10^{-5}	1.28×10^6	5.6×10^{-2}

organics should increase due to an increase in reaction sites for leaching to occur. However, if the pore surface area is unavailable to water, then the leaching of organics may be better explained by the $\log d_{32}$ surface areas.

According to the BET results, the greatest leaching of organics should occur with size distributions 1 and 2 which should be approximately the same while size distribution 3 should have the least amount of organic leached from coal. According to the $\log d_{32}$ results, the leaching of organics should be greatest for size distribution 3 and progressively less for distributions 2 and 1.

It should be noted that the BET and $\log d_{32}$ surface areas are just two of several methods available for determining surface area. Other methods for determining surface area are available and might be more suitable for explaining the leaching of organic compounds from coal.

C. Molecular Weight Analysis

The leachates from size distributions 1, 2, and 3 had NVTOC concentrations of 310 ppm, 320 ppm, and 304 ppm, respectively. The NVTOC concentration for size distribution 3 was concentrated to 304 ppm by vacuum distillation while the NVTOC concentrations for size distributions 1 and 2 were obtained by direct extraction. The column loading in micrograms of NVTOC were 930 μg , 960 μg , and 912 μg , respectively.

Figures 13-15 show the NVTOC elution profiles for the three size distributions. These profiles are essentially the same, showing only one significant peak which elutes over a volume from 240 ml to 330 ml of eluate. These profiles show that organic compounds eluted over a volume from 150 to 370 ml of eluate. The V_e values used to calculate the

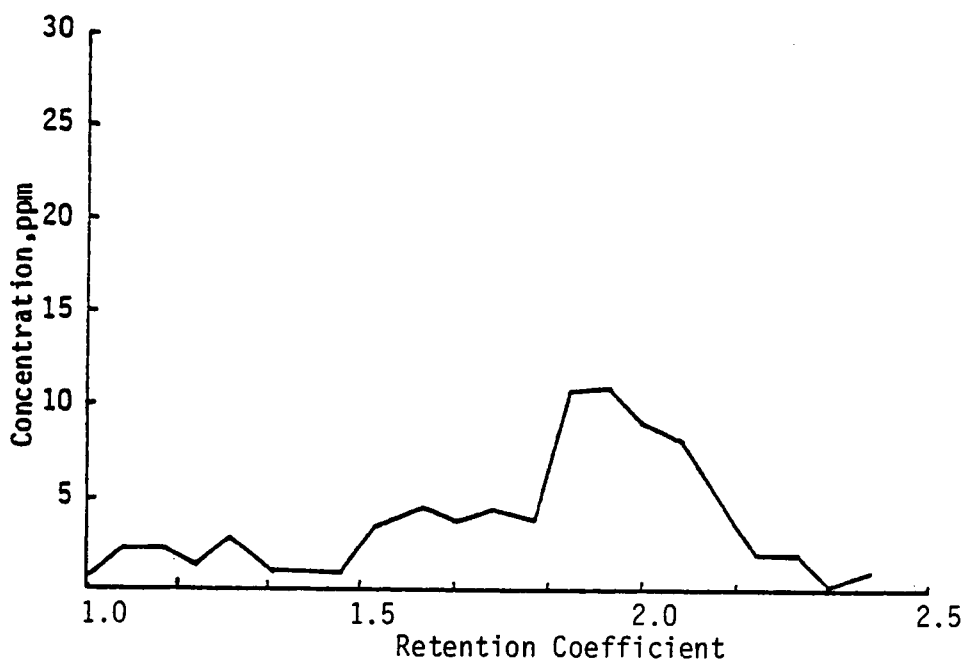


Figure 13. NVTOC profile for size distribution 1 leachate.

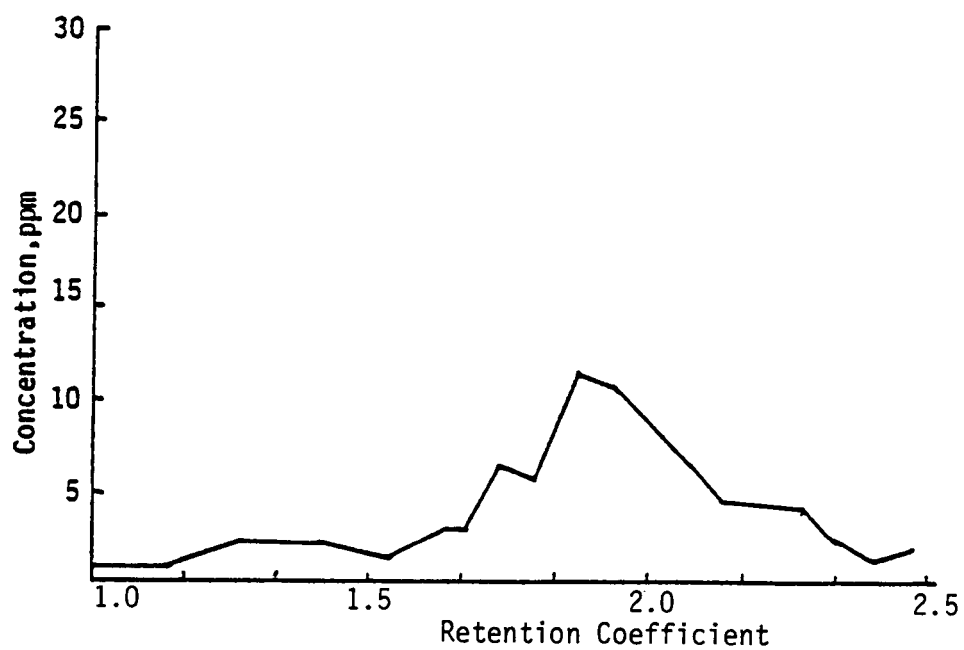


Figure 14. NVTOC profile for size distribution 2 leachate.

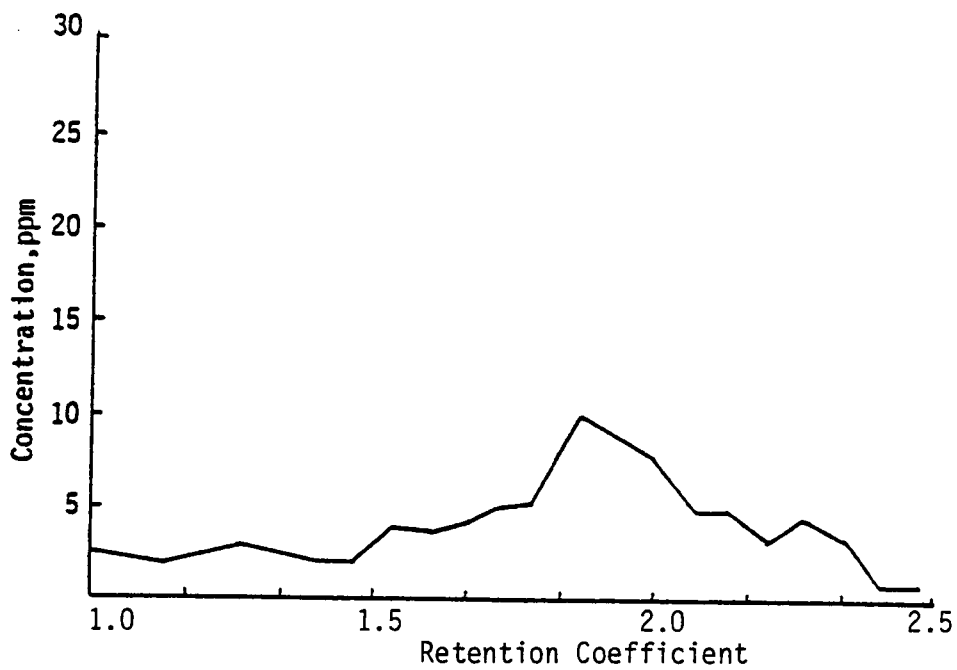


Figure 15. NVTOC profile for size distribution 3 leachate.

retention coefficient were 285 ml for size distribution 1 and 280 ml for size distributions 2 and 3. The retention coefficients were calculated by the equation $R = V_e/V_o$ and were calculated to be 1.9 for all three size distributions.

Ethylene glycol, which has a molecular weight of 62, was also analyzed on this column. The elution volume for this compound was 310 ml which gave an R value of 2.1. The close elution volumes between ethylene glycol and the organics present in the leachates indicate that most of these organic compounds have molecular weights close to 100.

A mass balance was done to assure that all of the injected NVTOC had eluted from the column. This was done by subtracting the eluted micrograms of NVTOC (corrected for background NVTOC) from the injected micrograms of NVTOC. Table 11 shows that 48 μg , 68 μg , and 32 μg of NVTOC for size distributions 1, 2 and 3 respectively, were not recovered which means approximately 95% of the injected NVTOC was recovered. This was probably due to analytical errors in measuring the NVTOC of the fractions. Therefore, from the mass balances, it is assumed that essentially all of the NVTOC has eluted.

D. Extraction Efficiency of C18 Resin, XAD-2 Resin, Tenax GC Resin, and Activated Charcoal

The overall extraction efficiency for the C18 Sep Paks varied from 1.0% to 20.0% with an average efficiency of 8.2%. A Pearson correlation test was performed to test if there was any correlation between the EXNVTOC and the extraction efficiency of a Sep Pak. This test showed no correlation between the two variables. The average extraction efficiency for samples containing extraction NVTOC levels of approximately 30 ppm was also 8.2%.

Table 11. Mass Balance for the Molecular Weight Analysis.

Size Distribution	Column Loading, μg	Eluted NVT0C, μg	NVT0C not Recovered, μg
1	930	882	48
2	960	892	68
3	912	880	32

The extraction efficiencies for XAD-2 resin, Tenax GC resin, and activated charcoal were 7.0%, 3.3% and 37.0% respectively. C18 resin, XAD-2 resin, and Tenax GC resin had approximately the same extraction efficiencies. This is not surprising since these adsorbents possess similar bonding mechanisms; Van der Waals bonding and π electron interactions for XAD-2 and Tenax GC resins; and Van der Waals bonding for C18 resin.

The surface loading for the XAD-2 resin, Tenax GC resin, and activated charcoal columns was $19.2 \text{ ug TOC/cm}^2 \cdot \text{minute}$ and was $10 \text{ ug TOC/cm}^2 \cdot \text{minute}$ for the C18 Sep Pak. These surface loadings were calculated using the initial TOC concentration of 30 ppm and an average flow rate of 0.5 ml/minute.

The higher extraction efficiency for the activated charcoal may be due to the additional bonding mechanisms it possesses. In addition to Van der Waals bonding and π electron interactions, activated charcoal also has hydrogen bonding and cation exchange mechanisms.

Figure 16 is a plot of the NVTOC concentration versus the volume of leachate passed through the adsorbents. It can be seen from this graph that the TOC concentration remained approximately the same from zero to 250 ml of leachate passed through the adsorbent. Although these adsorbents were not efficient for removing the total organic carbon, these graphs do show that the adsorbents were efficient for those compounds that were adsorbed from the leachate.

Until more is known about the organic compounds present in the leachate, it is difficult to explain the low extraction efficiencies of these adsorbents. Greater efficiencies may possibly be obtained by using larger extraction columns. However, since water was used to leach

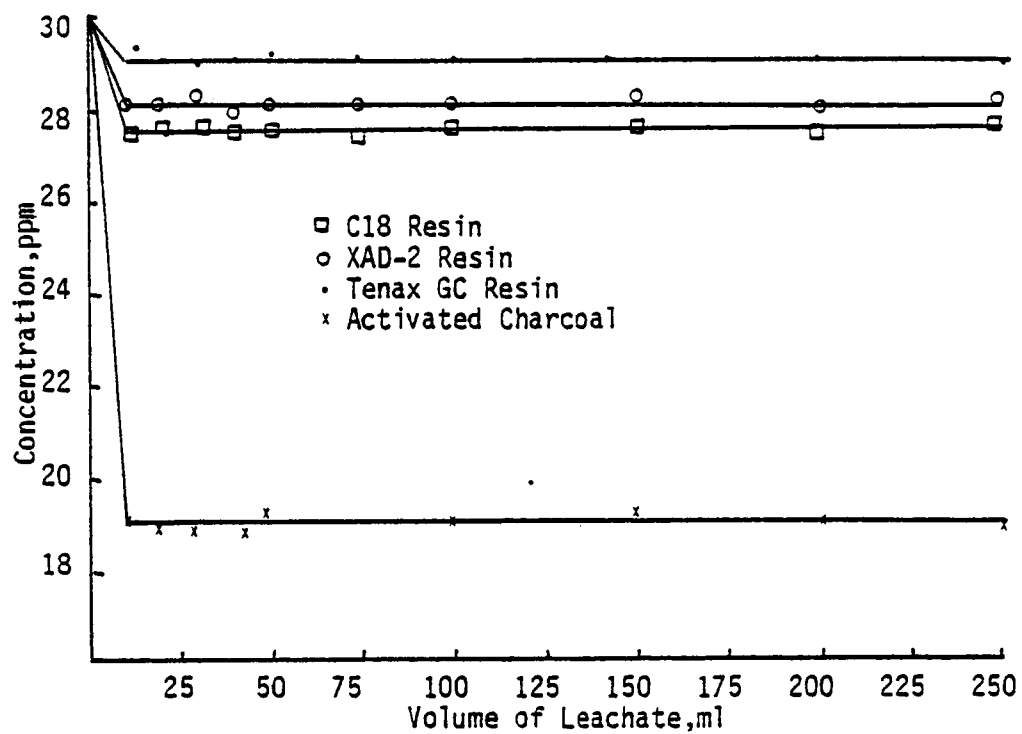


Figure 16. Removal of NVTOC by C18 resin, XAD-2 resin, Tenax GC resin, and activated charcoal.

the organics from coal, it is likely that a large percentage of the compounds present in the leachate are very polar which would make their extraction from water extremely difficult.

E. HPLC Results

HPLC Analysis of Phenols

Figure 17 shows the chromatograph of four known phenols; catechol, vanillin, phenol, and 8-quinolinol. The elution times for these compounds were 9.0, 11.0, 16.2, and 25.0 minutes, respectively. The concentrations of these compounds were; catechol: 0.2%, vanillin: 0.1%, phenol: 0.5%, and 8-quinolinol: 0.2%.

Comparing the elution times for the organic compounds extracted from the leachate, it can be seen that phenol and Peak 3 elute at approximately the same time. This indicates that peak 3 may represent compound(s) similar in structure to phenol. The early elution times for Peaks 1 and 2 indicate that these compounds are more polar than the other organic compounds (Peak 3 and the four phenols).

HPLC Analysis of Extracted Organic Compounds

Figure 18 presents a typical chromatogram of the acetonitrile eluate. The first three peaks represent organic compound(s) that were extracted from the leachate. The fourth peak shown on the chromatogram was 2-Napthol which was the internal standard.

The elution times for Peaks 1, 2, and 3 were typically 1.5, 3.5, and 15.0 minutes, respectively. Slight variations of 0.5 to 1.0 minutes did occur in some of the samples. The elution time for the internal

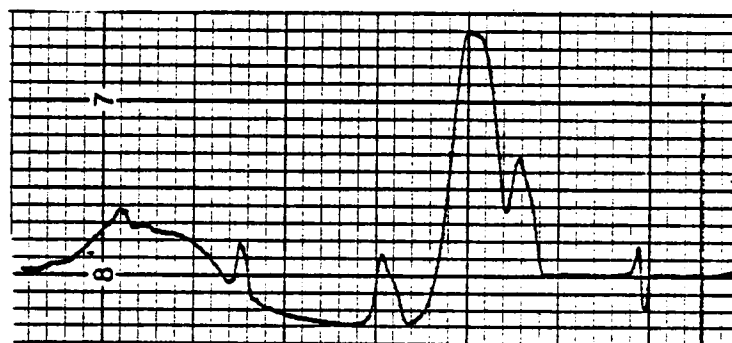


Figure 17. HPLC chromatogram of catechol, vanillin, phenol, and 8-quinilinol.

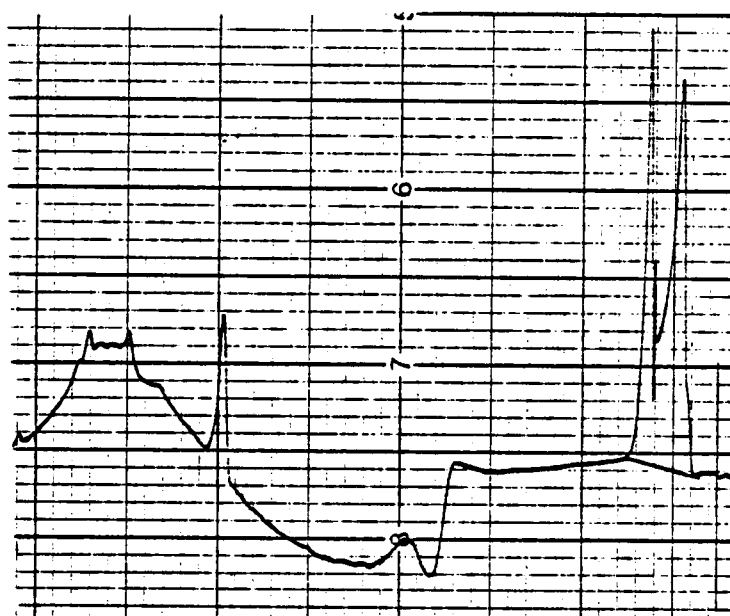


Figure 18. HPLC chromatogram of the extracted organic compounds.

standard, however, was more erratic. It varied from a low of 22.5 minutes to a high of 37.0 minutes. This variation in the internal standards elution times did not coincide with variations in the elution times for Peaks 1, 2, and 3 (i.e. a 50% increase in Peak one's elution time was not followed with a 50% increase in the internal standard's elution time).

The wide range of elution times for the internal standard may have been caused by variations in the flow rate or the solvent gradient, however, instrument checks on the pump and the solvent programmer showed no irregularities. It was noticed that as the number of chromatographic runs increased, the elution time for the internal standard generally increased. Column pressure was also observed to increase which indicates partial plugging of the column. Table 12 shows the number of runs and the elution times for the internal standard. Between runs 34 and 35, the column was cleaned with tetrahydrofuran using reverse flow through the column. This helped momentarily for six runs. Further cleaning did not help.

Three other possible explanations for the wide range of elution times for the internal standard are; (1) organic contaminants present in either the water or the acetonitrile affected the elution of the internal standard, (2) the HPLC column had not reached equilibrium between injections, (3) the organic compounds represented by Peaks 1, 2, and 3 affected the elution of the internal standard, and (4) organic compounds, which were irreversibly adsorbed onto the column or were difficult to remove from the column, changed the characteristics of the column.

Table 12. Elution Time for Internal Standard

Run #	Internal Standard Elution Time, minutes
1	24.0
2	25.0
3	25.0
4	25.0
5	24.5
6	24.5
7	24.5
8	25.5
9	24.5
10	24.5
11	24.5
12	24.5
13	24.5
14	26.5
15	31.5
16	31.5
17	26.8
18	27.5
19	27.5
20	28.0
21	35.0
22	35.0
23	30.5
24	30.4
25	30.0
26	31.5
27	32.0
28	32.0
29	32.0
30	32.0
31	32.0
32	28.0
33	28.0
34	28.0
35	22.5

Table 12 (Con't).

Run #	Internal Standard Elution Time, minutes
36	22.5
37	22.5
38	22.5
39	22.5
40	22.5
41	22.5
42	35.0
43	35.0
44	35.0
45	35.0
46	35.0
47	37.0
48	35.0
49	35.0
50	35.5

The peaks present on the chromatogram were measured according to their peak heights. These peak heights had units of absorbance units per millivolt (AU/mv) and were calculated by the following equation

$$[(\% \text{ Full Scale Peak Deflection})(1.0 \text{ AU})]/1.0 \text{ mv}$$

These heights were used to indicate the relative amounts of organics leached from coal. Absolute concentrations of the organic compounds could not be related to these heights because the identity and response factors of the organic compounds present in the leachate were unknown.

Tables 13 and 14 present the HPLC data obtained in this study. The data in Table 13 have not been normalized while the data in Table 14 have been normalized. According to Table 13 the peak height ranges were as follows; Peak 1: 0.10×10^{-2} AU/mv to 95.0×10^{-2} AU/mv; Peak 2: 0.0 to 22.5×10^{-2} AU/mv; Peak 3: 0.0 to 10.0×10^{-2} AU/mv. The normalized peak height ranges were; Peak 1: 0.08 to 12.00; Peak 2: 0.00 to 12.00; Peak 3: 0.00 to 1.13.

Effects of Particle Size and Coal Slurry

The ANOVA results for the normalized data are presented in Table 15. F values greater than 2.93 indicate that the percentage of coal in the slurry significantly affects the peak's response while F values greater than 3.33 indicate that the particle size distribution significantly affects the peak's response.

The results in Table 15 show that size distribution significantly affected the responses of Peaks 1 and 3 but not the response of Peak 1 and the Total Peak Response. In order to evaluate the size distribution effects, graphs of the mass mean diameters (M'_g) for distributions 1, 2, and 3 versus the normalized peak responses were made for Peaks 1 and 3.

Table 13. HPLC Data

Size Distribution	Slurry	Experiment	Peak Height, 10^{-2} AU/mv			Total Peak Response
			Peak 1	Peak 2	Peak 3	
1	A	1	4.5	4.0	6.8	15.3
		2	2.5	10.9	4.2	17.6
		3	1.0	7.0	5.0	13.0
		4	1.9	3.9	4.8	10.6
1	B	1	4.2	3.5	10.2	17.9
		2	1.0	6.8	3.5	11.3
		3	3.0	16.0	4.5	23.5
		4	1.2	5.7	3.4	10.3
1	C	1	9.0	9.0	9.0	27.0
		2	1.8	8.5	4.0	14.3
		3	5.5	12.5	5.5	23.5
		4	3.1	12.1	3.6	18.8
1	D [*]	1	95.0	22.5	0.0	117.5
		2	20.4	13.0	0.0	115.0
		3	42.5	0.0	0.0	42.5
		4	65.0	4.0	0.0	69.0
2	A	1	1.5	2.2	4.0	7.7
		2	0.5	3.0	5.0	8.5
		3	1.2	7.5	4.5	13.2
		4	5.0	0.0	5.0	10.0
2	B	1	2.0*	6.2	6.0	14.2
		2	0.5	0.5	0.5	1.5
		3	4.0	10.5	7.0	21.5
		4	7.0	1.0	6.5	14.5
2	C	1	3.5	8.7	5.5	17.7
		2	1.5	4.5	6.0	12.0
		3	5.0	5.5	5.5	16.0
		4	4.5	2.5	6.0	13.0
2	D [*]	1	35.0	0.0	0.0	35.0
		2	42.5	9.0	0.0	51.5
		3	22.0	10.8	0.0	15.3
		4	37.5	10.5	0.0	28.0

Table 13 (Con't).

Size Distribution	Slurry	Experiment	Peak Height, 10^{-2} AU/mv			Total Peak Response
			Peak 1	Peak 2	Peak 3	
3	A	1	1.7	12.8	3.0	17.5
		2	4.0	17.0	3.2	24.2
		3	15.5	15.5	2.5	33.5
		4	8.8	16.0	3.3	28.1
3	B	1	23.0	7.8	2.0	32.8
		2	32.5	8.8	1.0	41.8
		3	31.0	5.3	2.0	38.3
		4	35.5	2.2	1.0	38.7

* The peak heights for slurry D were multiplied by five

**missing data

Table 14. HPLC Normalized Data

Size Distribution	Slurry	Experiment	Normalized Response			Total Peak Response
			Peak 1	Peak 2	Peak 3	
1	A	1	0.39	0.33	0.43	1.15
		2	0.33	1.66	0.57	2.56
		3	0.10	0.69	0.51	1.30
		4	0.21	0.43	0.53	1.17
1	B	1	0.40	0.54	0.91	1.85
		2	0.14	1.15	0.48	1.77
		3	0.30	1.59	0.46	2.35
		4	0.15	0.71	0.43	1.29
1	C	1	1.03	1.34	0.81	3.18
		2	0.29	1.88	0.67	2.84
		3	0.57	1.27	0.56	2.40
		4	0.34	1.34	0.40	2.08
1	D	1	12.00	6.50	0.00	18.50
		2	11.50	4.00	0.00	15.00
		3	4.5	2.00	0.00	6.50
		4	1.20	2.40	0.00	8.00
2	A	1	0.19	0.54	0.50	1.23
		2	0.08	0.49	0.82	1.39
		3	0.29	0.59	0.95	1.83
		4	0.45	0.00	0.45	0.90
2	B	1	0.23	0.81	0.71	1.75
		2	**	.	.	.
		3	0.47	0.56	0.82	1.85
		4	0.35	0.00	0.43	0.80
2	C	1	0.38	0.91	0.64	1.93
		2	0.32	1.27	1.13	2.71
		3	0.77	0.55	0.85	2.17
		4	0.12	0.00	0.47	0.59
2	D	1	4.40	12.00	0.00	0.00
		2	3.00	0.00	0.00	3.00
		3	2.25	1.20	0.00	8.25
		4	2.00	0.00	0.00	2.00

Table 14 (Con't).

Size Distribution	Slurry	Experiment	Normalized Response			Total Peak Response
			Peak 1	Peak 2	Peak 3	
3	A	1	0.10	0.82	0.21	1.13
		2	0.31	1.18	0.26	1.75
		3	1.97	2.13	0.31	4.41
		4	0.73	1.33	0.28	2.34
3	B	1	2.28	0.98	0.19	3.45
		2	2.88	0.91	0.09	3.88
		3	3.39	0.38	0.15	3.92
		4	2.51	0.08	0.07	2.66

.** missing data

Table 15. Analysis of Variance Results for Normalized Data

Peak	Source	F	Significance*
1	Slurry	33.30	Y
	Size Distribution	7.46	Y
2	Slurry	5.24	Y
	Size Distribution	0.10	N
3	Slurry	30.50	Y
	Size Distribution	17.50	Y
Total	Slurry	15.20	Y
	Size Distribution	1.59	N

*Y = significant

N = not significant

The M'_g values were not used to evaluate the peak's response pattern, instead the BET surface areas and the $\log d_{32}$ surface areas were used to evaluate the response patterns. The M'_g values were used to facilitate the graphing. The points that appear on the graph represent average values for each slurry.

Figures 19 and 20 show that the effects of size distribution are not clear. According to the BET surface areas, the normalized response should be lower at 20.5 μ (size distribution 1) than at 290 μ and 820 μ (size distributions 2 and 3, respectively) and should be the same at 290 μ and 820 μ . For slurries A and B, the largest normalized response occurred at A and B, however the normalized response at 290 μ and 820 μ were approximately the same as expected. However for slurry D the response was much greater at 820 μ than at 290 μ .

For Peak 3 the response was lower at 20.5 μ for slurries A and B as expected, however, the response, after increasing at 290 μ , then decreased at 820 μ . Slurries C and D also showed decreased normalized responses at 820 μ .

Table 15 shows that the percentage of coal in the slurry significantly affected the normalized responses for Peaks 1, 2, 3, and the Total Peak response. Figures 21-24 show that as the percentage of coal in the slurry increases, the peak responses also increase. This was due to the increased organic matter available for leaching. Two exceptions do occur, however, for Peaks 2 and 3, the response showed a decrease for size distribution 3; and in Peak 3 the response actually decreased to zero at 50% coal slurry for size distributions 1 and 2. This was probably not the true response since only 50 ml of the leachate were obtained for analysis with this slurry instead of 250 ml.

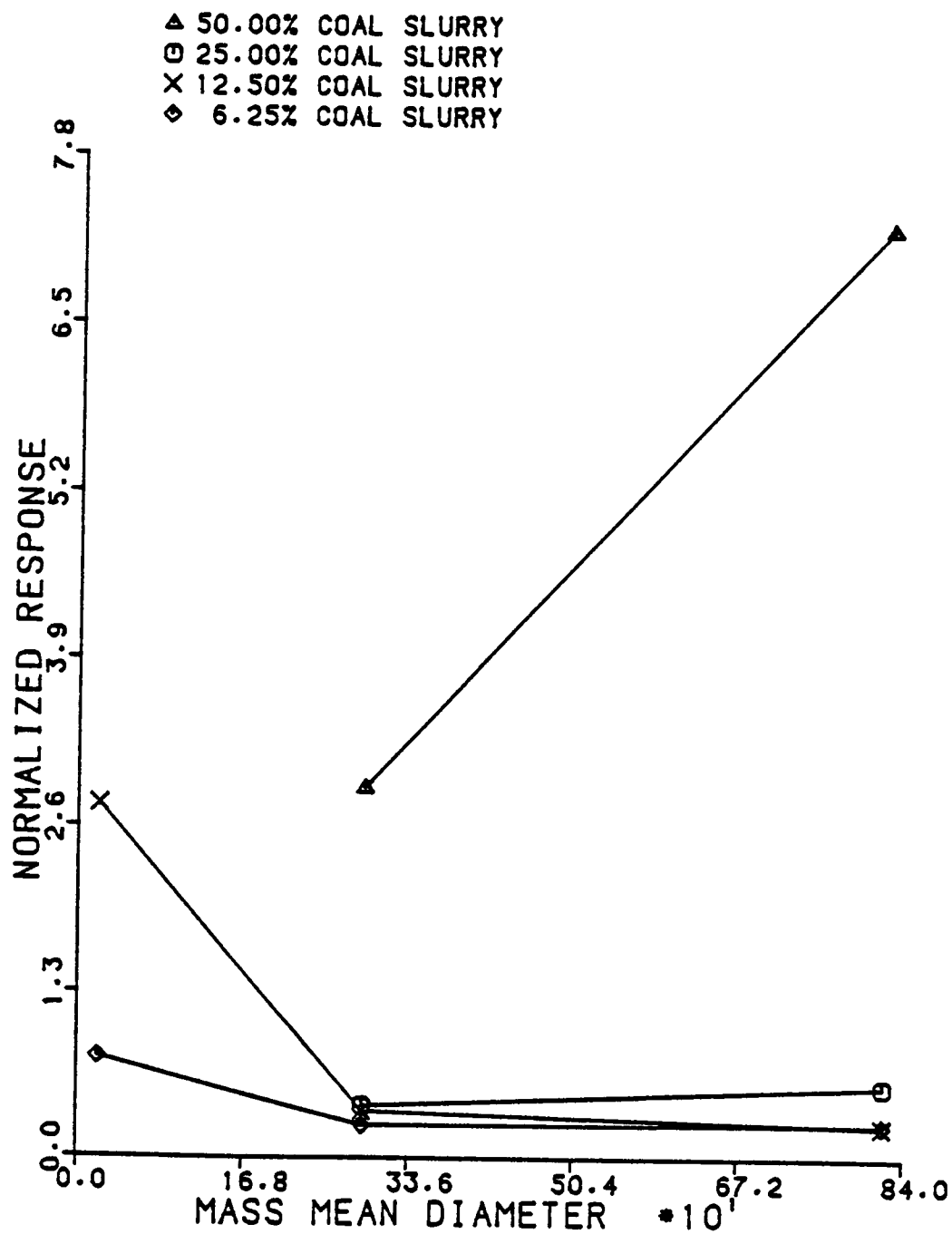


Figure 19. Influence of particle size distribution on Peak 1's response.

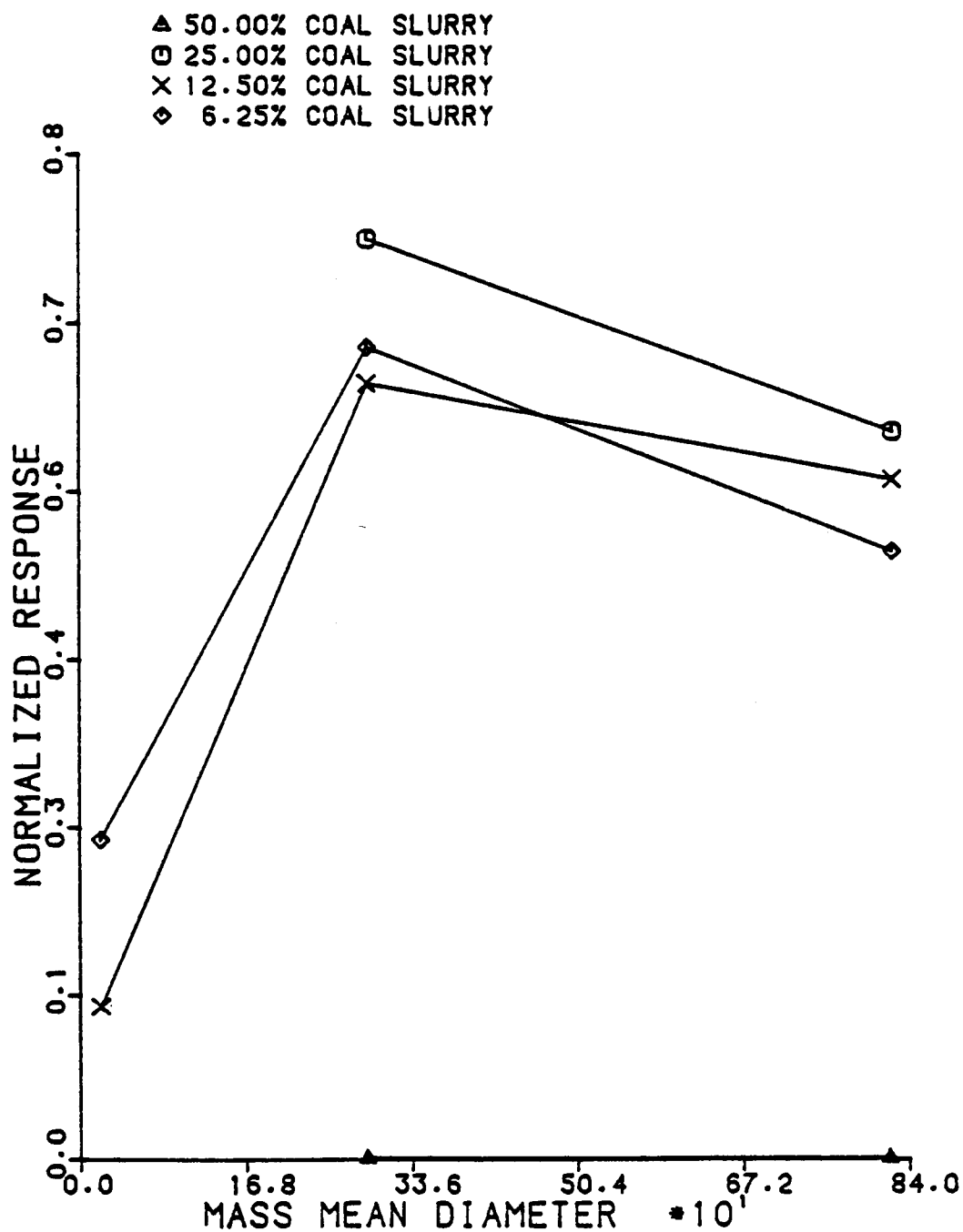


Figure 20. Influence of particle size distribution on Peak 3's response.

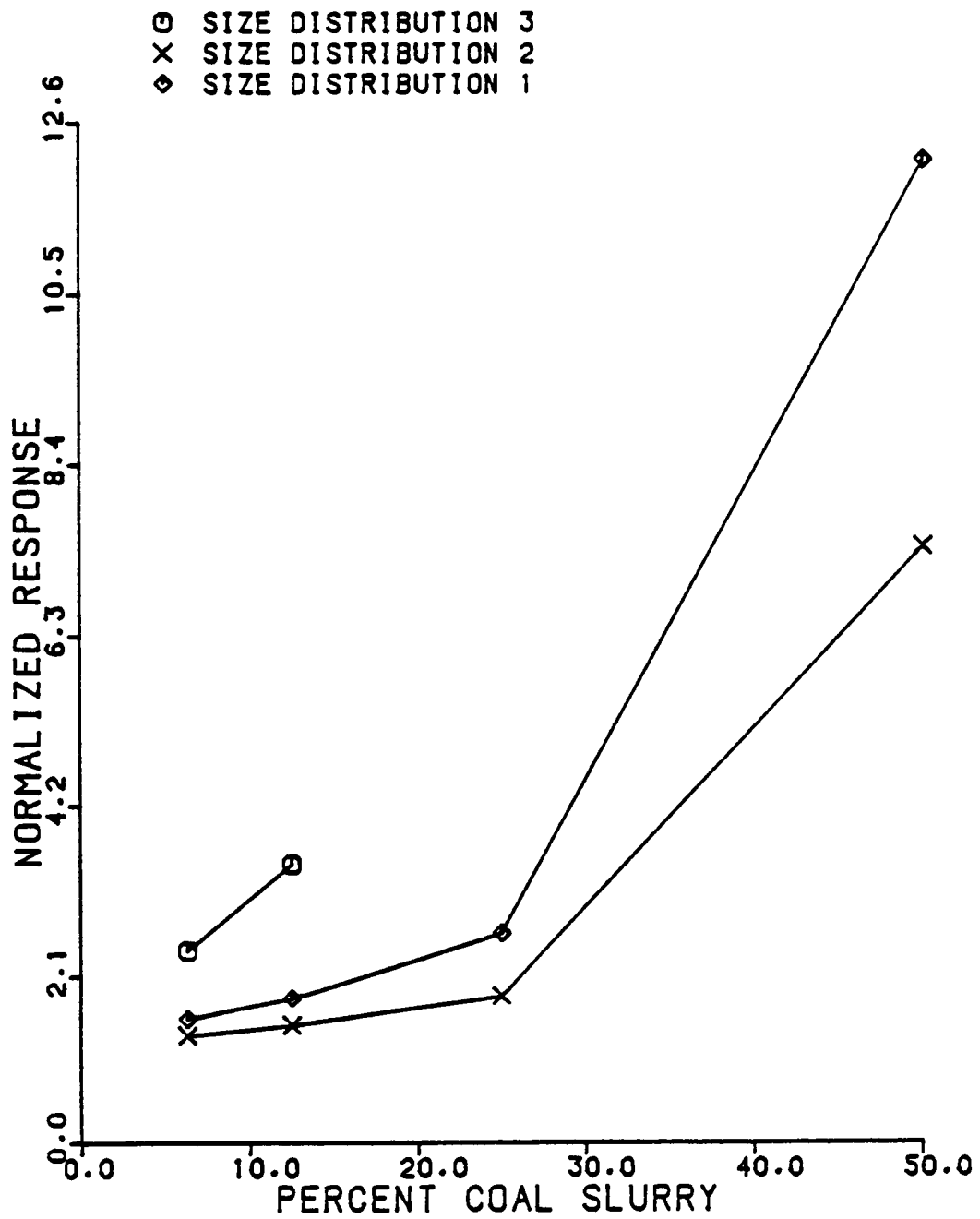


Figure 21. Influence of coal slurry on Peak 1's response.

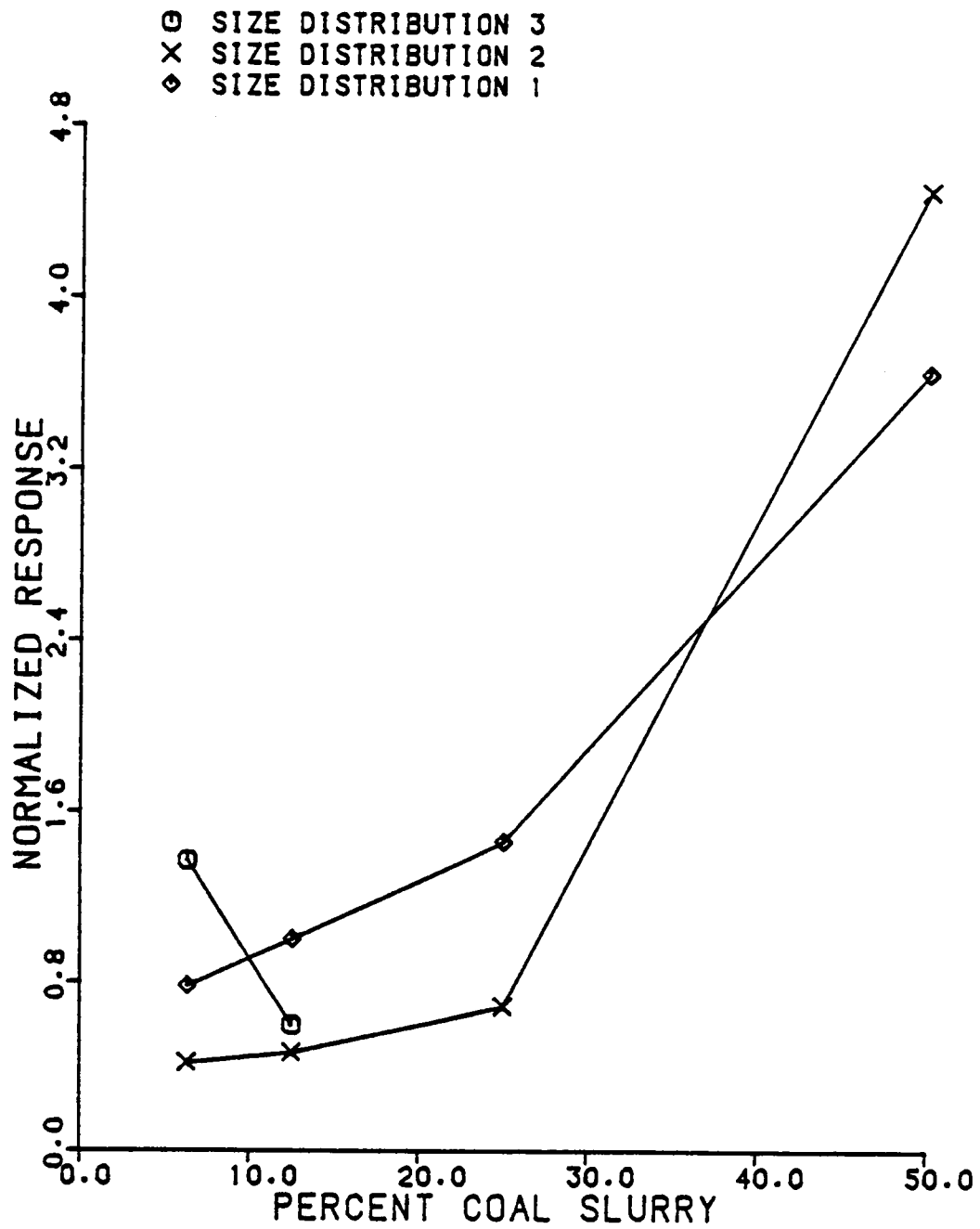


Figure 22. Influence of coal slurry on Peak 2's response.

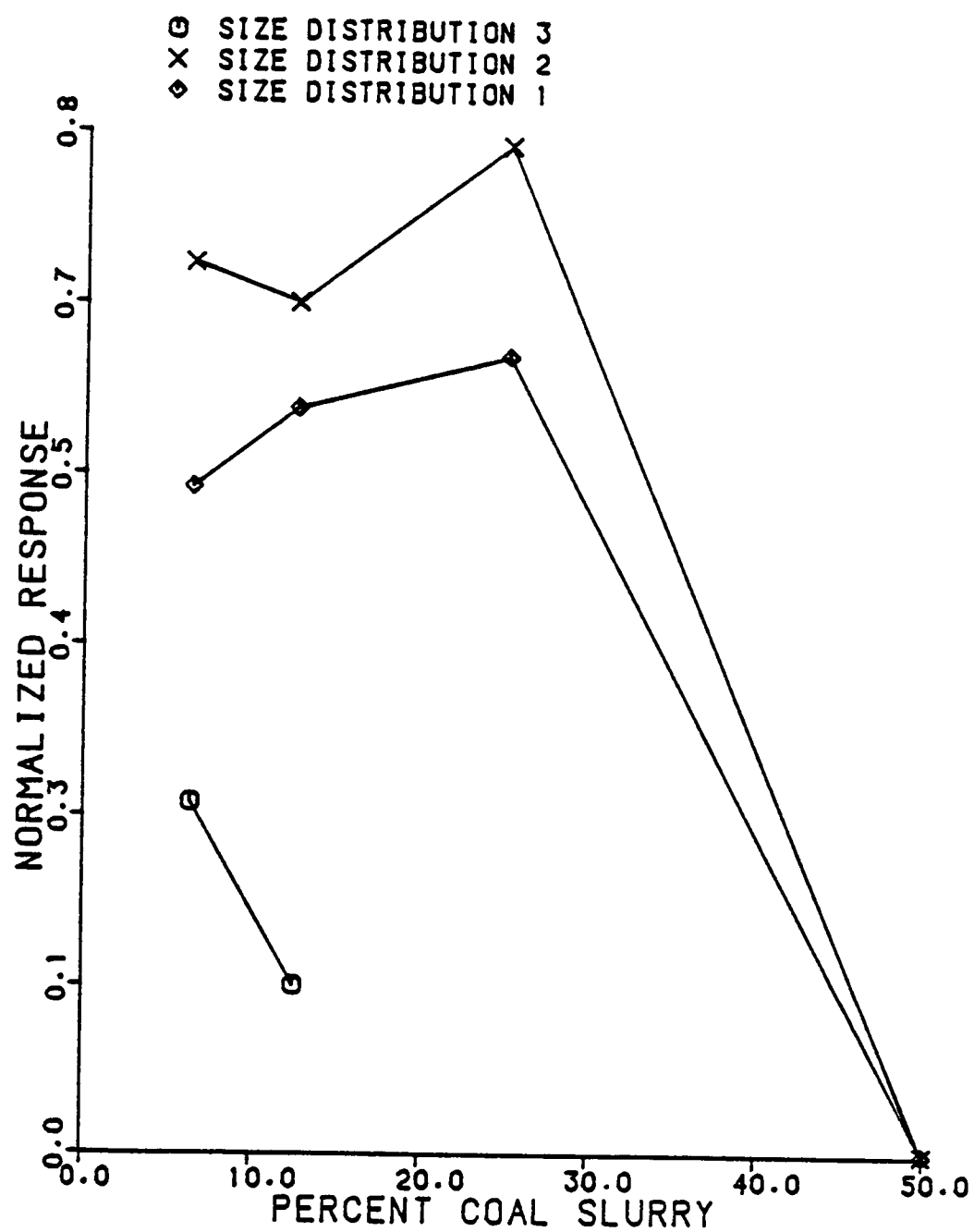


Figure 23. Influence of coal slurry on Peak 3's response.

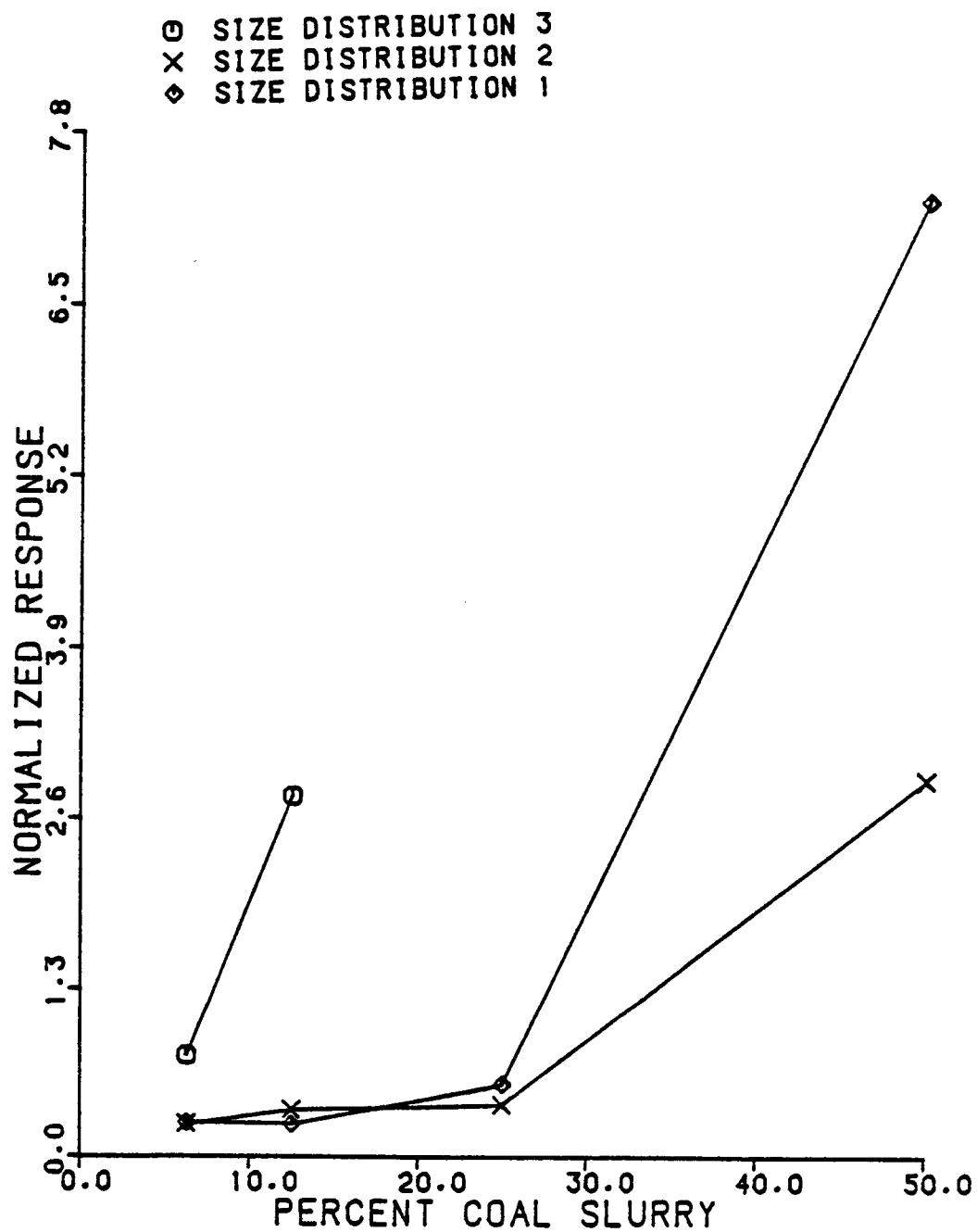


Figure 24. Influence of coal slurry on the Total Peak response.

These ANOVA results should be viewed with caution since the overall interaction efficiency for the C18 Sep Pak was low (8.2%) and the variation that occurred in this efficiency (1-20%). It is unusual that coal particle size does not significantly affect the INVTOC and EXNVTOC concentrations but does affect the normalized response of Peaks 1 and 3. This may be due to the low extraction efficiencies of the C18 Sep Paks and also to the variation in this efficiency. The inconsistent response patterns for these two peaks may also be due to the low extraction efficiency and variation in this efficiency.

F. Applications and Interpretations of Results

Characterization of the Organic Compounds Leached from Coal

Although the identities of the compounds leached from coal are unknown, information obtained from this study can be used to characterize what type of compounds may be present in the leachate.

The structure of coal presents an initial insight towards the nature of the compounds leached coal. Previous research has shown that (1) coal consists of an aromatic-aliphatic structure with three to five aromatic rings per lamella, (2) these ring clusters are joined together by either short aliphatic bridges, ether linkages, sulfide or disulfide bridges, or biphenyl bridges, (3) sulfur and nitrogen are incorporated into heterocyclic rings, and (4) oxygen exists mainly as hydroxyl and carbonyl groups.

From this knowledge of coal's structure, it is probable that the compounds leached from coal are heteroatom (nitrogen, sulfur, oxygen) containing aromatic compounds. Bond cleavage at the bridges between

ring clusters would result in compounds consisting of 3-5 rings which would result in compounds having molecular weights from approximately 300-500. However, the molecular weight analysis showed that most of the organic compounds present in the leachate were of relatively low molecular weight (approximately 100).

The HPLC analysis of these compounds indicates that these compounds have characteristics similar to aromatic compounds; (1) they absorbed light at a wavelength of 280 nanometers, and (2) they had elution times close to the elution times of phenol, vanillin, 8-quinolinol, and catechol. Peak three's elution time was actually the same as phenol.

Therefore, it can be hypothesized that most of the compounds present in the leachate are heteroatom (oxygen, sulfur, nitrogen) containing aromatic compounds of relatively low molecular weight (approximately 100).

Environmental Fate

The Federal Water Pollution Control Act (FWPCA) includes a toxic priority pollutant list of 129 compounds for which effluent guidelines are being developed. Many of these priority pollutants are aromatic compounds such as phenols and polycyclic aromatic hydrocarbons (PAH's); compounds which may be present in the leachate from coal piles and coal slurry pipelines. These wastewaters, therefore, may be subjected to various treatment processes should any of the organic compounds present in these wastewaters be classified as priority pollutants.

The fate of these compounds in the environment should be looked at before deciding whether or not treatment is necessary to control the levels of the pollutants in the wastestreams. If these compounds do not

persist in the environment, treatment to remove the compounds would not be needed.

Assuming that the compounds present in the leachate are aromatic compounds, several possibilities exist concerning their behavior in the environment. Once these compounds have been leached from coal, they may either remain in the water medium or enter either the soil or air media. The more polar compounds are more likely to remain in the water while the relatively nonpolar compounds are more likely to adsorb onto suspended particles or the bottom sediments. In both cases, these compounds may volatilize and enter the atmosphere.⁵⁴

Once in the environment, the compounds may either remain unaltered in their chemical forms or undergo degradation into less complex parts or complete breakdown to CO_2 , H_2O , and minerals.⁵⁴

Three mechanisms of degradation are possible; (1) biodegradation which is effected by living organisms, (2) photochemical degradation which is effected by light energy, and (3) chemical degradation which is effected by chemical agents.⁵⁴

Of these mechanisms, biodegradation and photochemical degradation are known to be important in the degradation of aromatic compounds in the environment.⁵⁵ The importance of each degradation mechanism depends upon the medium that the compound resides. Photochemical degradation is important in the atmosphere but is relatively unimportant in soil and water media unless the compound is located on the surface of water or soil. Biodegradation, however, is frequently the most important degradation mechanism in both soil and water media.⁵⁴

Biodegradation of Aromatic Compounds

Biodegradation (actually microbial metabolism) involves the breakdown of complex organic compounds into less complex components that can be utilized as energy sources for the synthesis of macromolecules necessary for microbial growth. In order for this to occur, the breakdown products of the complex compounds must be able to either directly or indirectly enter the tricarboxylic acid cycle (TCA) which provides energy for microbial synthesis of macromolecules (microbial anabolism).⁵⁴

The metabolic breakdown of aromatic compounds involves the cleavage of the aromatic nucleus which requires that the ring carry at least two hydroxyl groups either ortho or para to each other (Figure 25).⁵⁵ These substituents, if not already present on the ring, may be introduced by one of two enzymatic reactions; (1) monooxygenase reactions which introduces one atom of oxygen onto the aromatic nucleus, or (2) dioxygenase reactions which introduces two atoms of oxygen onto the aromatic nucleus. Once the aromatic nucleus has two hydroxyl groups either ortho or para to each other, ring cleavage is then possible and is accomplished by a dioxygenase enzyme. Three separate and distinct types of metabolic pathways are available for converting dihydroxyphenols into compounds capable of entering either directly or indirectly the TCA cycle; ortho and meta fission for catechols, and also the reactions involving the degradation of gentisic acids.⁵⁶ Examples of these fission pathways are shown in Figures 26, 27 and 28. Subsequent reactions convert the dicarboxylic acids into compounds incorporated into the natural metabolic cycles of the organism and are ultimately converted into carbon dioxide and water. These fission reactions are usually quite specific to the species of microorganism, thus the ability for the

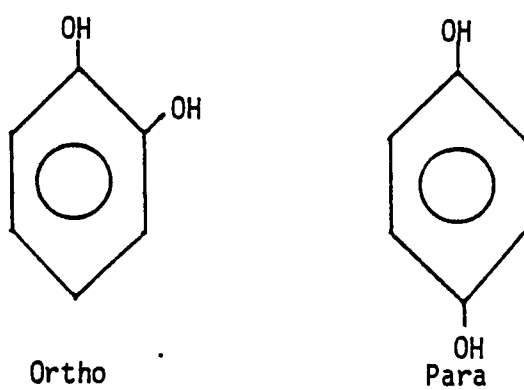


Figure 25. Ortho and para substituted benzene rings.

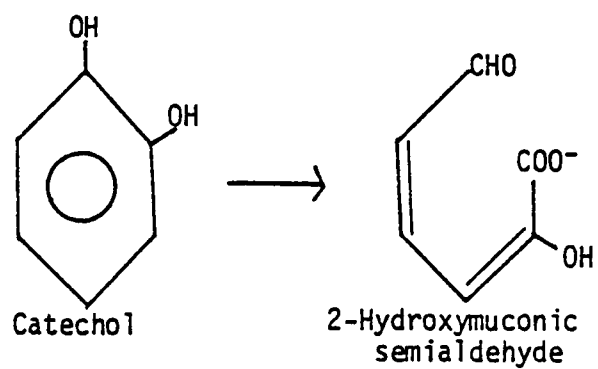


Figure 26. Ortho fission for catechol.

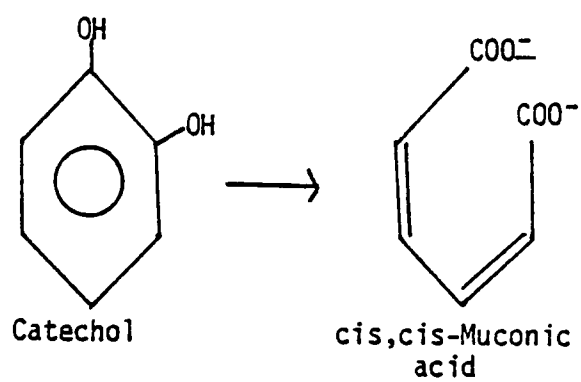


Figure 27. Meta fission for catechol.

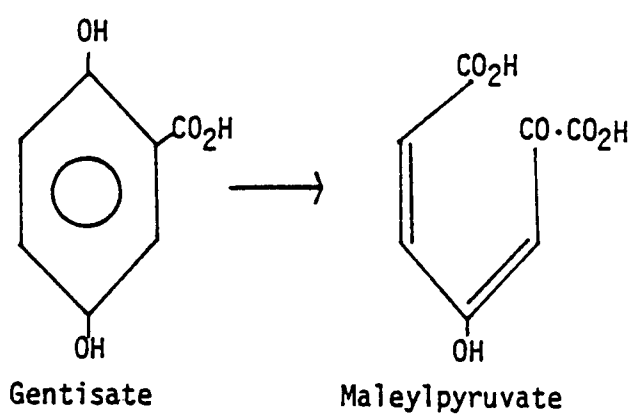


Figure 28. Fission of gentisate.

environment to degrade different types of compounds is dependent upon the heterogeneity of the microbial population.⁵⁵ Various aromatic compounds are susceptible to microbial attack including biphenyl, naphthalene, phenanthrene, and anthracene.⁵⁵

Since most of the compounds leached from coal are probably low molecular weight aromatic compounds, it is likely that these compounds are susceptible to biodegradation and would not require treatment before their release into the environment. However, the molecular weight analysis of the leachate showed that some higher molecular weight compounds are present in the leachate. As a general rule higher molecular weight compounds are less susceptible to biodegradation than lower molecular weight compounds. Therefore, treatment of the leachate may be necessary to remove the higher molecular weight compounds should they prove to be resistant to biodegradation. Possible future studies involving the leachate from coal piles and coal slurry pipelines could involve biodegradation studies to determine whether or not the extracted organic compounds are biodegradable. Tests which may be run on the leachate to determine biodegradability include Biochemical Oxygen Demand (BOD), Warburg procedure, and die-away tests.

Photochemical Degradation

Another possible degradation pathway for the aromatic compounds leached from Wyodak coal is through photochemical degradation. For photochemical degradation to occur, the compound of interest must absorb energy in the ultraviolet-visible (UV-VIS) range.⁵⁵ This absorption of energy results in the activation of an electron such that it moves from a lower energy orbital to a higher energy orbital. The most common

electron transitions corresponding to light energies in the UV-VIS range are from; $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ where n is a nonbonding electron occupied orbital, π is a bonding electron occupied orbital, π^* is an unoccupied antibonding pi orbital, and σ^* is an unoccupied antibonding sigma orbital. The relative energy levels for these orbitals are; $\sigma < \pi$ $n < \pi^* < \sigma^*$.

Functional chromophores in organic molecules that allow these transitions are; - O -, - S -, - Cl:, - Br:, - I:, - N -, > C = C <, - C $\equiv$ O: As a general rule, absorption in the UV-VIS range is most commonly associated with aromatic rings.⁵⁵

Once a compound has absorbed light it is said to be in an excited state and may either return to the original energy level or undergo chemical change. The compound may return to the ground state through loss of energy in the form of heat through collisions with other molecules or the energy may be released in the form of electromagnetic radiation (fluorescence or phosphorescence). Chemical changes that may occur are ionization, fragmentation, and isomerization. Ionization occurs through the loss of an electron from the compound. This is more commonly associated with high energy radiation such as gamma rays and X-rays. Fragmentation occurs when a bond breaks in a molecule forming two free radicals. Isomerization is the rearrangement of a molecule such as the transition of cis to trans isomers.

The active species formed after these reactions may then react with other compounds present in their environment such as oxygen and water. These reactions are called dark reactions.

Photochemical reactions may also occur through light absorbing catalysts. These compounds absorb light energy and transfer the energy

to other molecules which undergo photochemical reactions. Such reactions are called sensitized reactions.

A variety of photochemical reactions have been observed in the laboratory which may be important in the degradation of aromatic compounds in the environment, these are; photoisomerization, photosubstitution, and photooxidation. The photoisomerization of alkyl groups around a benzene ring has been observed by several investigators.^{57,58,59} These shifts do not involve photodissociation or recombination of the alkyl residues but a scrambling of the atoms of the benzene ring. Another example is photoisomerization of the chlorinated cyclodiene insecticides such as dieldrin, endrin, and aldrin.

The photosubstitution of aromatic compounds has been observed in a large number of halogenated pesticides. In general the substitution involves the rupture of the aryl halide bond to form a substituted aryl radical.⁶⁰ The fate of the radical depends upon the environment the radical is in. In a water and oxygen environment, a likely environment for the organic compounds leached from coal, the radical is generally oxidized to phenolic compounds although hydrogen substitution and dimerization have been observed.

Direct photooxidation has been observed in anthracenes, naphthalenes, and benzene.⁶¹ Anthracenes and naphthalenes are oxidized to transannular peroxides in the presence of oxygen. Benzene, in the presence of atomic oxygen, is oxidized to form phenol. In this reaction, UV irradiation of oxygen forms the atomic oxygen which then reacts with benzene.

Photosubstitution and photooxidation may prove to be instrumental in the degradation of aromatic compounds in the leachate. These reactions result in the addition of oxygen to an aromatic ring which is a very important step in the biodegradation of aromatic compounds.

Of these two degradation processes, biodegradation and photochemical degradation; biodegradation would probably be more important because the photochemical reactions only occur if the compounds are in the position to absorb sunlight. Since coal leachate is generally dark brown to black in color, light penetration would probably be low. Therefore, the only compounds which would be in position to absorb sunlight would be those located near the surface of the wastestream or those compounds with high vapor pressures which are more likely to evaporate into the atmosphere.

Treatment of the Coal Pile and Coal Slurry Wastestreams

Since the compounds present in the leachate are probably aromatic, there is a strong possibility that these compounds can be released into the environment with the subsequent degradation of these compounds into less complex components through either biodegradation, photochemical degradation, or both. Therefore, treatment to remove these compounds would not be necessary. However, if these degradation processes do not occur, then treatment of the wastestreams will be necessary.

One possible treatment method is the use of adsorbents to remove the TOC from the wastestreams. The extraction efficiency tests of the adsorbents, C18 resin, XAD-2 resin, Tenax GC resin, and activated charcoal, show that these adsorbents would not be efficient in removing the TOC from the wastestream. Of these adsorbents, activated charcoal was the most efficient and it had an efficiency of only 37%.

V. SUMMARY

HPLC analysis of the leachate revealed three peaks representing organic compounds extracted from the coal leachate. ANOVA analysis showed that coal particle size significantly affected the normalized response for Peak 1 and Peak 3 responses. These responses, however, could not be explained by either the BET nitrogen surface areas or the $\log d_{32}$ surface areas of the coal samples.

The percentage of coal present in the slurry was found to significantly affect the normalized response for all three peaks and the Total Peak response. Generally, the response of the peaks increased as the percentage of coal present in the slurry increased.

The BET nitrogen surface areas for coal samples with mass mean diameters of 820, 290, and 20.5 microns were 8.9, 8.8 and $2.9 \text{ m}^2/\text{g}$. The $\log d_{32}$ surface areas for these samples were 9.3×10^{-4} , 2.9×10^{-3} , and $5.2 \times 10^{-2} \text{ m}^2/\text{g}$.

The extraction efficiency for the C18 Sep Paks varied from 1 to 20% with an average extraction efficiency of 8.0%. The extraction efficiencies for XAD-2 resins, Tenax GC resin, and activated charcoal were 7.0, 3.3, and 37.0%, respectively. The extraction efficiencies were fairly constant over a volume of 10-250 ml of leachate.

Molecular weight analysis of the leachate showed that most of the organic compounds present in the leachate were of relatively low molecular weight ($\cong 100$).

Based on the molecular weight analyses, HPLC analyses, and the structure of coal, most of the organic compounds present in the leachate

are probably heteroatom (oxygen, nitrogen, and sulfur) containing aromatic compounds of relative low molecular weight ($\cong 100$).

Once released into the environment, these compounds may undergo biodegradation and photochemical degradation thus negating any treatment to remove these compounds from the leachate. The low extraction efficiencies of the four absorbents, C18 resin, XAD-2 resin, Tenax GC, and activated charcoal show that these absorbents would not be practical to remove the organic compounds from the leachate.

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